

INVESTIGATING THE POTENTIAL OF SURFACTANTS IN IMPROVING THE
PERFORMANCE OF STIMULATION FLUIDS IN ULTRA-TIGHT SHALES

A Thesis

by

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ABSTRACT

Commercial recovery of oil and gas from ultra-tight shale formations depends significantly on the performance of hydraulic fracturing. Enhancing the performance of the stimulation treatment can improve the estimated ultimate recovery of the well. This study investigates the potential of surfactants in enhancing the performance of hydraulic fracturing fluids by altering wettability and improving the process of spontaneous imbibition in oil rich shales demonstrating nanodarcy range permeability.

This study combines experimental work with numerical modeling and ties the lab findings to the wellhead performance in the field. A total of five different surfactants including nonionic and novel complex nano-surfactants were investigated in this study. Contact angle and interfacial tension measurements were performed at reservoir temperature to identify the state of native wettability and the impact of surfactants in altering wettability. Thereafter, spontaneous imbibition experiments were performed using computed tomography methods to understand the improvement in the magnitude of imbibition penetration due to surfactant addition. Overall, the complex nano-surfactants were more efficient in altering the wettability of the shale samples as compared to the nonionic surfactants. However, the results of the spontaneous imbibition experiments showed that one of the nonionic surfactants was just as effective in improving oil recovery as the complex nanosurfactants.

Core scale numerical modeling was performed to explain the experimental findings and the results of the core scale model were used in a single well frac model to

investigate the impact of wettability alteration due to surfactant on well performance after hydraulic fracturing. It was observed that addition of surfactant to frac fluid lowers cumulative oil recovery due to the presence of additional capillary force resulting from a preferential state of wettability, which counteracts the viscous force created by the applied pressure drawdown.

The potential of surfactants in altering wettability in ultra-tight shales was verified in this study. Although wettability alteration during well stimulation was not found to be beneficial to the primary well performance, it might prove to be useful in other applications such as surfactant enhanced oil recovery in shales.

DEDICATION

This thesis is an outcome of all those life experiences which have molded me into the person I am today. I dedicate this thesis to my mother who spent countless hours praying for my success and well-being, my father who taught me important life lessons and inspired me to work hard towards success, my elder brother who has been a constant pillar of unconditional help and support, my late grandfather, who served as my real life role model, and my wonderful girlfriend, Crystal, who inspired and comforted me during testing times. I would also like to dedicate this thesis to family and friends, and all the people who have supported me throughout my academic career and encouraged me to achieve my goals.

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1. INTRODUCTION

Hydraulic fracturing and horizontal well drilling are inarguably the two most instrumental practices that have resulted in America's shale revolution. Hydraulic fracturing is a fairly common stimulation technique in the industry today and is applied in both conventional and unconventional reservoirs to achieve production enhancement. Fracturing of rock is not a new concept and has been known for over hundred years. Fractures can occur naturally in the earth crust along with dikes, joints, and faults due to natural earth processes (Pollard 1978; Pyrak-Nolte et al. 1987) or they can be created artificially by human operations. Although fracturing by the process of hydraulic fracturing is usually desirable, other operations like drilling can also induce unintentional fractures in the rock (Aadney and Bell 1998).

The process of hydraulic fracturing can be explained as a chain of events where a hydraulic fracturing fluid is pumped at a high pressure and rate to initiate and subsequently propagate a crack (or fracture) in the subsurface rock. In general, once the rock is cracked, sorted sand (termed as "proppant") is placed in the fractures to keep them open (Coker and Mack 2013). This process results in the stimulation of the well which in turn improves the productivity of the well due to the increased surface area of the wellbore and improved flow geometry around the well (Advani et al. 1985). Although, the first application of hydraulic fracturing was in form of a acidizing job in the 1930's which resulted in enhanced well production (Veatch and Moschovidis 1986), the first commercial non-acid fracturing treatment was performed in 1947 in the

Hugoton field which reported an improvement in well performance (Veatch 1983). The practice gained popularity in the early 1950s and it was viewed as an important stimulation treatment for secondary recovery. Valko and Economides (1995) reported that since 1950s, over 70% of the gas wells and 50% of the oil wells have been hydraulically fractured in the US. **Fig.1** shows the performance of one such well hydraulically fractured in 1955 after being completed in 1951. Post fracturing, the production rate was reported to jump from 4 bopd to 130 bopd (Paul and Taylor 1958).

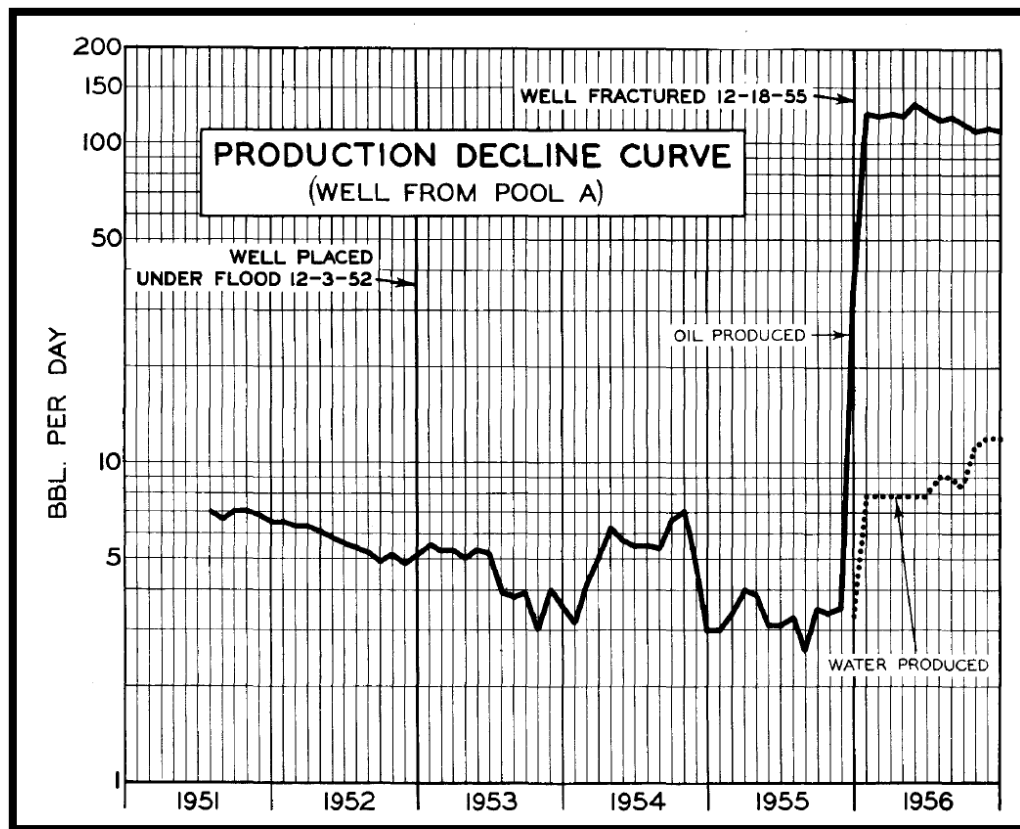


Fig. 1—Impact of hydraulic fracturing on the well production decline (Paul and Taylor 1958)

Hydraulic fracturing started out as a mere stimulation treatment but with the industry shifting its focus towards unconventional reservoirs with low and ultra-low permeability; it has evolved as a necessary treatment for primary recovery. Permeability ranging from several microdarcies to a few nanodarcies is not uncommon today, and economic production from such tight reservoirs is only possible with a comprehensive fracturing treatment. A typical hydraulic fracturing job can be divided into four major stages. In the first stage, a large volume of fluid also called the “pad” is pumped into the producing formation to create the fractures (Roudakov 2006). In the next stage, a slurry of fracturing fluid combined with proppant is pumped into these fractures. The role of proppant is to keep the fractures open after the end of the treatment when the formation resorts to its initial pressure. This is followed by the “flush” stage where a clean fluid is pumped to clean the subsurface tubulars and equipment. The final step is the “flowback” stage where the well comes online and the fracturing fluid is typically flowed back to the well.

A successful hydraulic treatment requires careful planning and proper design of the treatment. Proppant selection is a complicated issue which strongly influences fracture conductivity (Montgomery and Steanson 1985). The components of the fracturing fluid depend on the type of hydraulic fracturing treatment planned. In recent times, the two popular categories of fracturing fluid systems have been crosslinked and linear gel systems, and slickwater systems. Either system is comprised of more than 99.5% water. Slickwater systems are fairly basic and only one or more compounds among a friction reducer, clay stabilizer, biocide, and surfactant are added to the water

(Palisch et al. 2010). The gel based systems usually have a few more components in them. A typical crosslinked fracturing fluid system contains water, clay stabilizer, friction reducer, gelling agent, crosslinker, breaker, buffer, biocide, and surfactant (Montgomery 2013).

A surfactant is a component which can reduce the interfacial tension between the fracturing fluid and the formation fluid and/or alter the wettability of the formation matrix. Surfactants have been studied extensively in the literature. However, most of these studies have focused on the use of surfactants in chemical enhanced oil recovery (EOR) processes. Surfactant flooding is an established chemical EOR process which had gained popularity in the late 20th century. Surfactant flooding had showed immense potential in the lab. However, several disappointing field trials and high cost of chemicals resulted in this technique receiving a cold shoulder in the industry (Jakobsen and Hovland 1994). Although, active research on surfactant-aided imbibition is currently going on, these projects are typically geared towards conventional reservoirs (Adejare et al. 2012; Babadagli 2003; Bortolotti et al. 2010; Celik and Somasundaran 1980; Delshad et al. 2009a; Gupta and Mohanty 2008; Li et al. 2004; Pinto 2013; Seethepalli et al. 2004; Shubham et al. 2012; Wang and Mohanty 2013; Zheng and Rao 2010). Similar research on surfactant-aided imbibition in unconventional reservoirs is limited. Although surfactants routinely feature as a component in a typical fracturing fluid system, its impact on ultra-tight liquid rich shales is not clearly understood.

Wang et al. (2012) performed a study on core samples from three Bakken wells in different parts of the Williston Basin in North Dakota to understand the potential of

surfactants to improved oil recovery in the Bakken. The results obtained in her study indicated great potential of surfactant in improving imbibition and increasing oil recovery. Although, this work claimed to describe the impact of surfactant on ultra-tight shale, the permeability of the cores used in the experiments was reported as 40 microdarcies. Shale reservoirs with permeability in the nanodarcy range are not uncommon today. There has not been any published literature which discusses the effectiveness of surfactant in improving imbibition and increasing oil recovery in oil rich shale reservoirs with nanodarcy range permeability. This research investigates the potential of surfactants in improving imbibition and increasing oil recovery in such shale reservoirs with ultralow permeability.

1.1 Research Objectives and Overview of Thesis Sections

The objective of this research is to investigate and compare the potential of various surfactants to alter wettability in ultra-tight oil rich shale reservoirs and improve the process of imbibition to increase estimated ultimate recovery (EUR). Specifically, the research aimed at achieving the following objectives:

- a) Evaluate and compare the ability of surfactants in fracturing fluid to alter wettability in ultra-tight shale cores by conducting contact angle and interfacial tension (IFT) measurement experiments at reservoir conditions
- b) Use computed tomography (CT) to quantify depth of fracturing fluid spontaneous imbibition by analyzing CT response before, during, and after the spontaneous imbibition experiment and measuring oil expulsion

- c) Build a core scale numerical simulation model to model surfactant enhanced fracturing fluid imbibition and oil recovery in the core experiments
- d) History match core scale spontaneous imbibition experiments and compare the performance of different surfactants
- e) Build a field scale simulation model to represent a hydraulically fractured single horizontal well with multistage fracturing
- f) Use results obtained from core scale surfactant imbibition simulation runs in the single well simulation model and compare surfactant potential in improving wellhead performance
- g) Identify surfactant which provides optimum performance for use in stimulation treatments in the ultra-tight oil rich shale reservoirs

This thesis is divided into nine sections. Section 2 presents a summary of relevant work available in the literature. The similarities and dissimilarities of various works to this research have been presented and discussed. Section 3 provides a short description of the workflow applied in this research and also offers background information pertinent to the reservoir studied in this research. Section 4 describes the contact angle measurement experiments and presents the results. Section 5 discusses the methods and results from the interfacial tension (IFT) experiments. Section 6 provides the complete discussion of the spontaneous imbibition experiments using CT methods while Section 7 describes the aspects of numerical modeling of the experimental results. Section 8 applies the results of section 7 to numerically investigate surfactant imbibition

in ultra-tight shales at a larger scale and lastly, Section 9 presents the summary of the work done and wraps it up with conclusions and recommendations for future work.

2. LITERATURE REVIEW

As mentioned at the end of Section 1, not a significant volume of literature directly related to this novel research is available at this point. Hence, the literature review on this subject primarily comprises of the work conducted on the area of surfactant aided imbibition in conventional carbonate and naturally fractured reservoirs, along with discussion on the fundamental mechanisms involving surfactants. Literature pertinent to the experimental approaches used in this study has also been reviewed. Besides, a part of this section is dedicated to discussion of the modeling aspects of surfactant aided imbibition.

2.1 An Introduction to the Role of Surfactant in the Fracturing Fluid

A surfactant is added to a fracturing fluid in order to reduce the IFT between the fracturing fluid and the formation fluid and/or alter the wettability of the formation rock. Wettability is defined as the “tendency of one fluid to spread onto a solid surface in the presence of other immiscible fluids” (Anderson 1986b; Green and Willhite 1998). The molecular interactions between the fluids and the solid surface dictate the state of wettability. The molecules of the fluid which form a stronger bond with the solid surface tend to spread on the surface to minimize the energy of the system (Anderson 1986a). This results in that fluid wetting the rock in the presence of the other immiscible fluid. Physical parameters such as temperature and pressure along with the composition of the fluids, the roughness and mineralogy of the rock affect the strength of the molecular forces and result in different degrees of wettability (Vijapurapu and Rao 2003).

Although wettability is highly sensitive to temperature, it is affected to a much lesser extent by changes in pressure (Okasha and Al-Shiwaish 2010; Wang and Gupta 1995). Wettability plays an important role in oil recovery processes especially in the presence of fractures. The distribution and flow of oil and water in the reservoir during are strongly influenced by the wettability of the system (Morrow 1990). It is also safe to assume that only oil and water compete to wet the rock as in the presence of gas, gas is always the non-wetting phase in the system (Anderson 1987).

Imbibition is the process of the displacement of the non-wetting phase by the wetting phase into the capillary pores of the rock matrix (Babadagli 2003). The process is a function of wettability, IFT, density difference, and pore size (Chen et al. 2001; McCaffery and Mungan 1970). The mechanism of imbibition has the potential to play a huge role in improving the performance of hydraulic fracturing treatments and increasing oil recovery from oil rich shale reservoirs. The addition of surfactant can favorably alter the wettability of the formation rock and allow strong spontaneous imbibition of fracturing fluid into the rock matrix subsequently expelling oil from the matrix into the hydraulic fractures, thus, improving performance and EUR.

2.2 The Concept of Wettability

2.2.1 Measurement of Wettability

It is a rather difficult task to measure wettability of a system. Although several methods have been proposed in the literature, the three major quantitative tests proposed by Anderson (1986b) for wettability determination are:

- a) Contact angle measurements

b) Amott-Harvey index

c) USBM method

2.2.1.1 Contact Angle Measurements

Contact angle method can be used to quantify wettability when a specific surface is in question. Amott-Harvey and USBM methods provide the average wettability of a volume such as a core. The contact angle method is ideal when the surface of the rock is flat and fairly smooth. Surface roughness can hugely affect the measured contact angle results and the apparent contact angle can differ significantly from the true contact angle (Morrow 1975). Different methods have been suggested to measure contact angles such as tilting plate method, sessile or pendant drop method, vertical rod method, tensiometric method, cylinder method, and capillary rise method (Adamson 1982; Good 1979; Johnson and Dettre 1969; McCaffery 1972; Neumann and Good 1979; Popiel 1978). In order to quantify wettability in this research, the pendant drop method was used to measure contact angles as it is known to report fairly accurate contact angles and is fairly simple to apply (Wang and Gupta 1995).

2.2.1.2 Amott-Harvey Index

The Amott-Harvey index provides an indication towards relative water or oil wetting tendencies of the reservoir rock. The idea is that the wetting fluid will generally imbibe into the rock spontaneously displacing the non-wetting fluid. Once the spontaneous imbibition phase is over, a centrifuge is used to apply further force to let the wetting forcefully displace the non-wetting fluid.

The experiments is usually started with a core sample flooded or centrifuged in water first, and then in oil to obtain initial water saturation, S_{wi} . At this point, the Amott-Harvey test, which comprises of four basic measurements, is performed to measure the wettability of the sample (Glover 2001). The four measurements are shown in **Fig.2**.

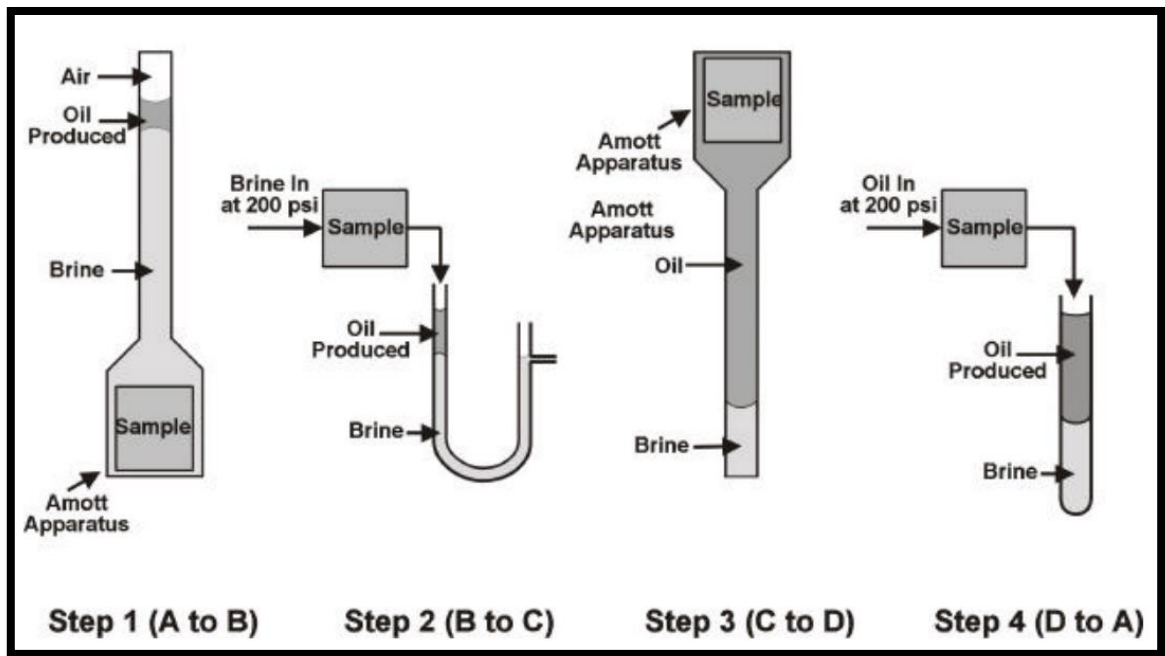


Fig. 2—Steps involved in the Amott-Harvey method (Glover 2001)

The amount of water spontaneously imbibed is measured during AB. The amount of water forcibly imbibed is obtained during BC. The amount of oil spontaneously imbibed is obtained during CD and DA provides the amount of oil forcibly imbibed. Once these measurements have been taken, the Amott-Harvey index can be calculated using Eq. 1.

$$Index = \frac{\text{Spontaneous Water Imbibition}}{\text{Total Water Imbibition}} - \frac{\text{Spontaneous Oil Imbibition}}{\text{Total Oil Imbibition}}$$

$$Index = \frac{AB}{AC} - \frac{CD}{CA} \dots \dots \dots (1)$$

Fig.3 shows a graphical representation of the Amott-Harvey method and the change in capillary pressure associated with each step.

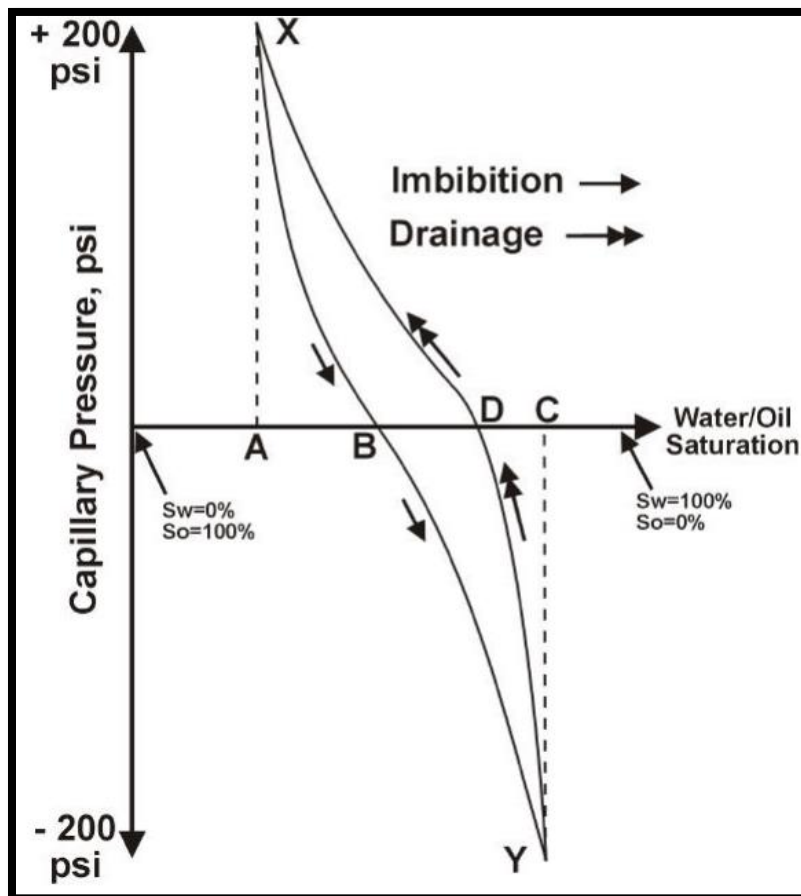


Fig. 3—Amott-Harvey wettability test data showing capillary pressure change associated with each step (Glover 2001)

2.2.1.3 USBM Method

The USBM method is very similar to the Amott-Harvey method (Glover 2001). The only difference lies in the fact that this method considers the work required to perform imbibition in the Amott-Harvey method. This test is usually carried out in a centrifuge, and the wettability index, W is calculated by applying Eq. 2 to area under the capillary pressure curves in Fig.3.

$$W = \log \frac{A_1}{A_2} \dots \dots \dots (2)$$

where A_1 is the area contained by XAD and A_2 is the area contained by YCB.

The problem with both the Amott-Harvey method and the USBM method is that they do not provide an absolute measurement of wettability. However, these two methods are the industry standard for comparing the wettability of different core plugs.

2.2.2 Types of Wettability

This classification is based on the preferential wetting tendencies of fluids on a certain solid rock and does not refer to homogenous vs. heterogeneous wettability. A solid surface can demonstrate three kinds of wettability behavior as shown in **Fig.4**.

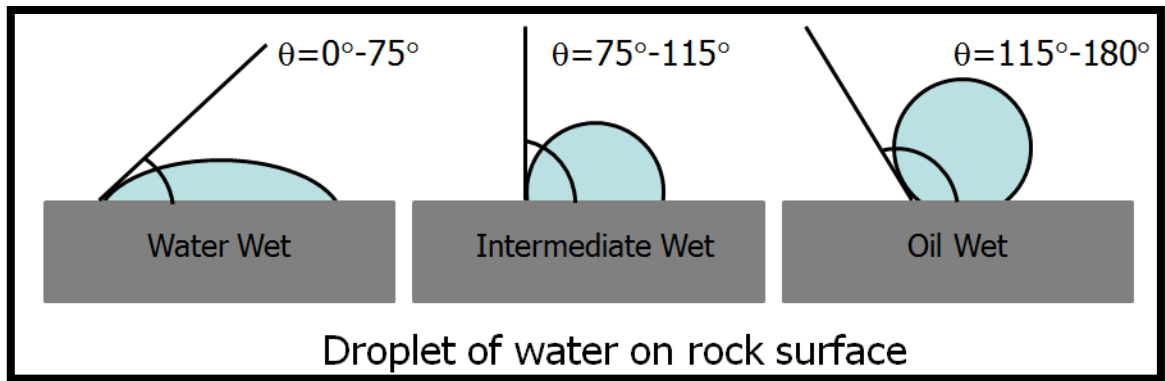


Fig. 4—Types of wettability

The rock surface could be considered as water-wet if the contact angle of the water droplet is between 0 and 75 degrees. If the water droplet beads up and shows a contact angle between 115 and 180 degrees, it is considered to show oil wettability. There is a case where neither fluid wets the rock preferentially, and this scenario is known as intermediate wettability. The contact angle for intermediate wettability ranges from 75 to 115 degrees (Reed and Healy 1984). However, it is important to note that different researchers have claimed different ranges of contact angles for a certain type of wettability in the literature.

2.2.3 Impact of Wettability on Spontaneous Imbibition and Capillary Pressures

2.2.3.1 Spontaneous Imbibition

Spontaneous imbibition is the process in which imbibition occurs naturally due to capillary pressure and/or gravity when a solid surface comes in contact with a fluid. Usually the wetting fluid imbibes spontaneously into the matrix resulting in the increase of the wetting phase saturation. If a core is water-wet, water will attempt to imbibe into

the core and displace the oil in the pores. The role of a surfactant is to shift the wettability of the system towards water wetness in order to allow water to efficiently imbibe into the matrix displacing the oil in place (Shuler et al. 2011).

In the event that external pressure is applied to aid in the process of imbibition, it is known as forced or dynamic imbibition. Although the process of forced imbibition is important for conventional systems and naturally fractured reservoirs, it becomes less relevant when dealing with ultra-tight rocks since, it is almost impossible to push anything through these rocks without actually just breaking them (Mohan et al. 2013).

2.2.3.2 Factors Affecting Spontaneous Imbibition

Spontaneous imbibition is a result of the combination of the capillary and gravity forces acting on the system. Wettability is the biggest factor in deciding the performance of the imbibition process. Apart from wettability, permeability, heterogeneity, fluid saturations, IFT, fluid viscosity and density, and thermodynamics can impact the process of spontaneous imbibition.

2.2.3.2.1 Permeability

Permeability is an important parameter which dictates the rate of imbibition. Spontaneous imbibition has always been considered an important recovery mechanism in low permeability reservoirs since viscous forces in such reservoirs are weak. Mattax and Kyte (1962) found that imbibition rate was directly related to permeability. Morrow (1976) concluded that if imbibition is gravity dominated, increase in permeability will lead to higher recovery since it seems to follow Darcy's flow equation in such a situation. However, Cuiec et al. (1994) claimed that experiments showed fast oil

recovery for strongly water-wet chalk even at low permeability. Zhou et al. (2000) showed that in their experiments on Berea cores that imbibition was highly sensitive to wettability and spontaneous imbibition is possible a wide range of permeability.

2.2.3.2.2 Heterogeneity

Although, it is a recognized fact that heterogeneity strongly impacts reservoir performance, the effect of heterogeneity on spontaneous imbibition has not been well established in the literature. Torsaeter (1984) conducted some experiments of water imbibition in chalk from the Ekofisk field and discussed some possible effects of micro-heterogeneities of permeability, pore structure, and surface roughness on the imbibition performance. Hamon and Vidal (1986) documented that their failure to match the imbibition performance of their numerical model to the actual oil recovery was due to micro-heterogeneities in the core plugs.

2.2.3.2.3 Fluid Saturations

The impact of initial wetting phase saturation has been researched extensively in the literature. Zhou et al. (2000) found from their experimental work that a decrease in initial water saturation resulted in a decreased water-wetness. However, Standnes and Austad (2000) claimed that in their wettability alteration experiments, initial water saturation in chalk had little influence on the imbibition process. The wettability alteration was concluded as a rate determining process. In other words, no definitive relationship between initial saturation and spontaneous imbibition has been established.

2.2.3.2.4 IFT

The impact of IFT will be discussed more in detail in a following section which will describe capillary pressure. Austad and Milter (1997) found that a decrease in IFT significantly decreases the rate of imbibition while performing experiments to compare the performance of an IFT reducing surfactant to brine.

2.2.3.2.5 Fluid Viscosity and Density

In the event of a large density difference between the fluids, gravity imbibition can become a major recovery mechanism. Allan and Sun (2003) showed that the density of oil was directly related to the recovery factor in their experiments with fractured reservoirs.

The relationship between the rate of imbibition and viscosity has been studied by many researchers and it has been shown that fluid viscosity is critical to the rate and extent of imbibition in the matrix (Ma et al. 1999; Zhou et al. 2002). Zhang et al. (1996) claimed that spontaneous imbibition is inversely proportional to the geometrical mean of the oil and water viscosity in water-wet sandstone rock. This claim was further bolstered theoretically by Zhou et al. (2002).

2.2.3.2.6 Fluid Viscosity and Density

As discussed previously, temperature impacts wettability and spontaneous imbibition significantly as it impacts all fluid flow parameters in a porous medium (Rao 1999). Carbonate rocks have shown to have the tendency to have improved water imbibition at higher temperatures (Wang and Gupta 1995), and sandstone rock have

been shown to have decreased water imbibition with an increase in temperature (Rao 1999).

2.2.3.3 Capillary Forces and the Concept of Capillary Pressure

The process of spontaneous imbibition as described in 2.2.3.1 is majorly driven by capillary forces. Capillary forces originate from the fact that the pore of the reservoir rock act like capillaries. In the presence of two immiscible fluids in a capillary, a capillary pressure is generated which impacts the process of imbibition. The relationship between capillary pressure, IFT, contact angle, and pore radius is given by the Young-Laplace equation as shown in Eq. 3.

$$P_c = P_{nw} - P_w = \frac{2\gamma \cos \theta}{r} \dots \dots \dots (3)$$

where P_c is capillary pressure, P_{nw} is non-wetting phase pressure, P_w is wetting phase pressure, γ is IFT, θ is contact angle, and r is pore radius of the rock.

In a water-wet system, the contact angle value would be lesser than 90 degrees indicating a positive capillary pressure according to Eq. 3. An oil-wet system gives a contact angle greater than 90 degrees resulting in negative capillary pressure values.

In order for a rock to imbibe water, the capillary pressure has to be higher than zero as that indicates water wetness. The lower the value of θ , stronger is the water-wetness. This is due to the fact the value of capillary pressure increases as $\cos \theta$ increases due to a decrease in the value of θ .

Austad and Milner (1997) had found that a decrease in IFT decreases the rate of imbibition. This can also be explained using Eq. 3. A decrease in IFT reduces the

capillary pressure of the system and hence, the rate of imbibition which is dependent on the capillary pressure of the system, slows down.

In conclusion, stronger water-wetness results in a high capillary pressure system and that allows effective and significant imbibition of water.

2.2.3.1 Spontaneous Imbibition Scaling Approach

The interplay of capillary, viscous, and buoyancy forces in determining the movement of fluids in the reservoir has been established by Morrow (1979). In spontaneous imbibition experiments, the impact of viscous forces is negligible as there is no applied pressure difference. The combination of capillary and buoyancy forces act as the predominant recovery mechanism. Many researchers have attempted to characterize and scale spontaneous water imbibition in crude oil/brine/rock (COBR) systems (Babadagli 1997, 2000; Babadagli 2001b; Behbahani and Blunt 2004, 2005; Delshad et al. 2009b; Galeh-Kalaei et al. 2013; Hamon and Vidal 1986; Hatzignatiou et al. 2012; Li and Horne 2002a, 2002b, 2004, 2006; Ma et al. 1995; Mattax and Kyte 1962; Mogensen and Stenby 1998; Morrow et al. 2002; Nurkamelia and Arihara 2004; Olafuyi et al. 2007; Saad et al. 1995; Sharma et al. 2011; Stoll et al. 2007; Stoll et al. 2008; Xie and Morrow 2000; Youssef et al. 2010; Zhang et al. 1996; Zhou et al. 2013).

One of the classical scaling approaches was presented by Mattax and Kyte (1962) in which they assumed that gravity forces are negligible and the oil/water viscosity ratio, initial fluid distributions, relative permeability functions, and capillary pressure are unchanged between models during the scaling process. Eq. 4 shows the Mattax and Kyte (1962) scaling method.

$$t_d = Ct \sqrt{\frac{k}{\varphi}} \frac{\sigma}{\mu_w} \frac{1}{L^2} \dots \dots \dots (4)$$

where t_d is dimensionless time, C is the unit conversion factor ($C=0.018849$), t is the time elapsed during imbibition in minutes, k is permeability in md, φ is porosity, σ is IFT in dynes/cm, μ_w is the viscosity of water in cp, and L is the length of the core plug.

Xie and Morrow (2000) presented a scaling approach which included the gravity forces in the equation (Eq. 5).

$$t_d(c + g) = t \frac{\frac{k}{\varphi}}{L_c^2 \sqrt{\mu_w \mu_o}} \left(\frac{\sigma}{\sqrt{\frac{k}{\varphi}}} f(\theta) + \frac{\Delta \rho g L_c^2}{L} \right) \dots \dots \dots (5)$$

where $t_d(c + g)$ is dimensionless time with both capillary and gravitational forces accounted for, and $f(\theta)$ is the wettability factor. In order to quantify the individual contribution of the gravity and capillary forces, Schechter et al. (1994) suggested the use of the inverse bond number (Eq. 6).

$$N_B^{-1} = C \frac{\sqrt{\frac{\varphi}{k}} \sigma}{\Delta \rho g L} \dots \dots \dots (6)$$

where N_B^{-1} is the inverse bond number and C is a dimensionless constant for capillary tube model ($C=0.4$). Schechter et al. (1994) proved that capillary forces are the dominating recovery mechanism for $N_B^{-1} > 5$. Gravity forces dominate in the system when $N_B^{-1} \ll 1$. If the inverse bond number falls in the range of 0.2 to 5, then the oil recovery is due to both capillary and gravity forces.

A more recent scaling method was proposed by Li and Horne (2004) in which they included the effects of IFT, wettability, initial saturation, and gravity forces. In this method, an attempt was also made to consider the effect of phase relative permeability. Although they validated their model using a one dimensional imbibition model, there this work clearly highlighted their assumption that the imbibition process was piston-like. The scaling method is shown in Eq. 7.

$$t_d = c^2 \frac{\lambda_w P_c}{\phi} \frac{S_{wf} - S_{wi}}{L_c^2} t$$

$$c = \frac{\Delta \rho g L}{(S_{wf} - S_{wi}) P_c} \dots \dots \dots (7)$$

2.3 Altering Wettability in Reservoir Rock

2.3.1 Wettability Alteration by Crude Oil

Wettability alteration by crude oil is a process that occurs during the migration of oil into the reservoirs. Carbonate and reservoirs are considered to be water-wet initially and are saturated with water. Wettability alteration can occur when the oil that migrated into these rocks interact with the rock surface in the presence of water. Literature suggests that the adsorption of heavy oleic and polar components of crude oil on the rocks can result in wettability alteration to oil-wetness (Donaldson and Alam 2008; Wang et al. 2011). Experimental work has shown that oil composition plays the most important role in determining wettability alteration by crude oil followed by reservoir temperature, rock composition and pressure (Buckley et al. 1998; Kumar et al. 2008; Standnes and Austad 2003). Initially water-wet rock samples were treated and aged with oil of varying compositions in these works and the extent of wettability modification was

analyzed for each case. Buckley et al. concluded that wettability alteration by crude oil was a result of four different processes as shown in **Fig.5**. These four processes are summarized as follows:

- a) Adsorption of oleic and polar components on to the rock surface in the absence of a water film resulting in the alteration of wettability from water-wet to oil-wet
- b) Precipitation of asphaltene on the rock surface due to the crude oil acting as a solvent resulting in alteration of wettability to weakly water-wet
- c) Instability of the water film on the rock surface and the potential of polar components in the crude oil to get adsorbed on the rock surface and alter wettability due to unique acid/base interactions which control the charges at the oil-water and water-solid interface
- d) Ion binding between high valence ions and highly charged sites resulting in wettability alteration to an oil-wet state

Fig.6 shows the process of wettability alteration due to adsorption of oleic and polar components. The polar components in crude oil get adsorbed onto the rock surface which is initially covered by water molecules. Once adsorption of crude oil happens, a rinse with a lighter crude results in the retention of an altered state of wettability.

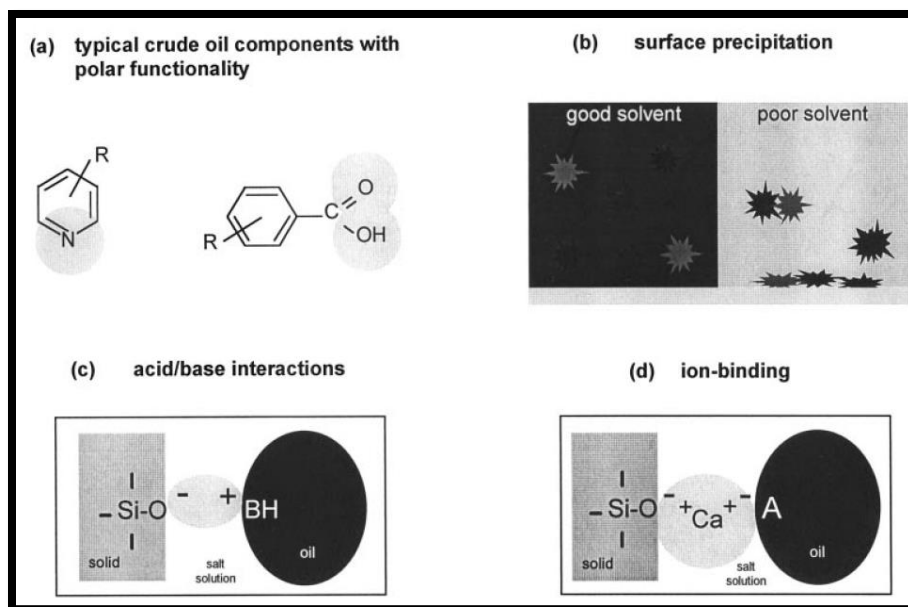


Fig. 5—Mechanisms of interaction between crude oil components and solid surfaces resulting in wettability alteration by crude oil (Buckley et al. 1998)

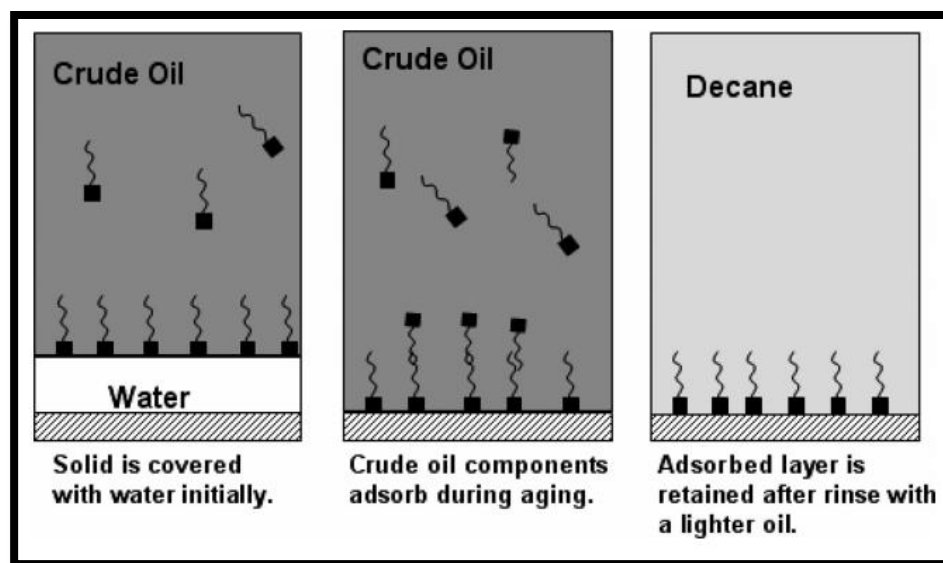


Fig. 6—Development of oil wettability due to the adsorption of the oleic components onto the rock surface (Buckley et al. 1998)

The complex polar interaction between oil and the rock surface was intensively studied by Thomas et al. (1993). They investigated the interaction of different oleic components containing fatty acids, carboxylic acids, sulfates and carboxylate polymers with calcite, dolomite and magnesite samples. Their investigation concluded that the change of wettability towards oil-wetness depends on the adsorbed quantity of oleic compounds on the solid surface and the hydrophobic features of the adsorbent. Wu et al. (2008) observed that the structure of the adsorbent also impacts the degree of wettability alteration by crude oil. The structure of naphthenic acid molecules dictates the process of wettability alteration. Higher the electrostatic attraction between the adsorbent and the mineral surface and the ability to form tight packing on the substrate, greater wettability alteration was observed in these experiments. In conclusion, adsorption of acidic components of oil on the solid surface is understood as the primary cause of wettability alteration towards preferential oil-wet state in majority of the reservoirs.

2.3.2 Wettability Alteration by Surfactants

2.3.2.1 Surfactant Chemistry

Surface active agents, better known as surfactants are amphiphilic compounds that contain partly hydrophilic and partly lipophilic components in a single molecule. The hydrophilic part is commonly known as the “head” group and the lipophilic part is called the “tail”. There are four broad categories of surfactants based on the charge of the head group present in the molecule as follows:

- a) **Anionic surfactants:** These surfactants have a negatively charged head group for example, phosphates, carboxylates, stearates, sulfates, and sulfonates

- b) Cationic surfactants: These surfactants have a positively charged head group for example, quaternary ammonium organics, pH-dependent primary, secondary, or tertiary amines, pyridium, piperidinium, and sulfonium compounds
- c) Non-ionic surfactants: These surfactants do not possess a net charge in the head group and are composed of long chain alcohols for example, alkyl-, alkyl-aryl, acyl-, acylamido-, acyl-aminepolyglycol ethers, polyoxy- glycol alkylphenol ethers, and glycerol alkyl esters
- d) Zwitterionic surfactants: These surfactants have both cationic and anionic centers attached to the head group giving it both positive and negative charges for example, aminocarboxylic acids and cocamidopropyl hydroxysultaine

Eksborg and Lagerstrom (1973) showed that the anionic and cationic surfactants can form ion-pairs and these ion-pairs have shown to act as the mechanism that can result in the alteration of wettability in reservoir rock. Cationic surfactants have shown enhancement in oil recovery by wettability alteration in oil-wet chalk and carbonate rocks (Austad et al. 1998; Sharma and Mohanty 2013; Zhang and Austad 2005). Anionic and non-anionic surfactants have also been studied and have been reported to be successful in altering wettability and improving oil recovery in fractured carbonate and chalk rocks (Adejare et al. 2012; Adibhatla and Mohanty 2008; Adibhatla et al. 2005; Chabert et al. 2010; Gupta and Mohanty 2010; Gupta and Mohanty 2008; Kumar et al. 2008; Nurkamelia and Arihara 2004; Olafuyi et al. 2007; Rao et al. 2006; Seethepalli et

al. 2004; Sharma and Mohanty 2013; Sharma and Mohanty 2011; Shubham et al. 2012; Wang et al. 2012; Weiss and Xie 2007). Hence, it is important to understand the underlying mechanism which results in wettability alteration due to surfactant in order to optimize the oil recovery process.

2.3.2.1 Wettability Alteration by Surfactant Adsorption

Standnes et al.(2000) showed oil recovery improvement in chalk cores with the use of anionic surfactants. Several other studies have claimed improved oil recovery from oil-wet cores due to the use of anionic surfactants (Adibhatla et al. 2005; Chen et al. 2000; Gupta et al. 2008; Gupta and Mohanty 2008; Hirasaki and Zhang 2004; Standnes and Austad 2000). Adibhatla et al. (2005) recovered oil using three different alkyl propoxylated sulfate surfactants. The difference in recovery between the brine only experiments and the surfactant experiments was huge with the anionic surfactants able to produce over 60% of the oil in 900 days as compared to brine only which recovered less than 5% oil. Hirasaki and Zhang (2004) showed that a dilute anionic surfactant with alkali recovered oil from aged dolomite cores. These studies suggested that anionic surfactants were able to alter wettability and improve oil recovery. Austad and Milner (1997) claimed that the anionic surfactant molecules altered wettability by creating a monolayer on the rock surface through hydrophobic interactions with the lipophilic tail of the adsorbed crude oil components on the rock. **Fig.7** shows the formation of the monolayer due to the adsorption of the surfactant molecules with the hydrophilic head group oriented outward of the surface causing the wettability alteration to a preferential water-wet state.

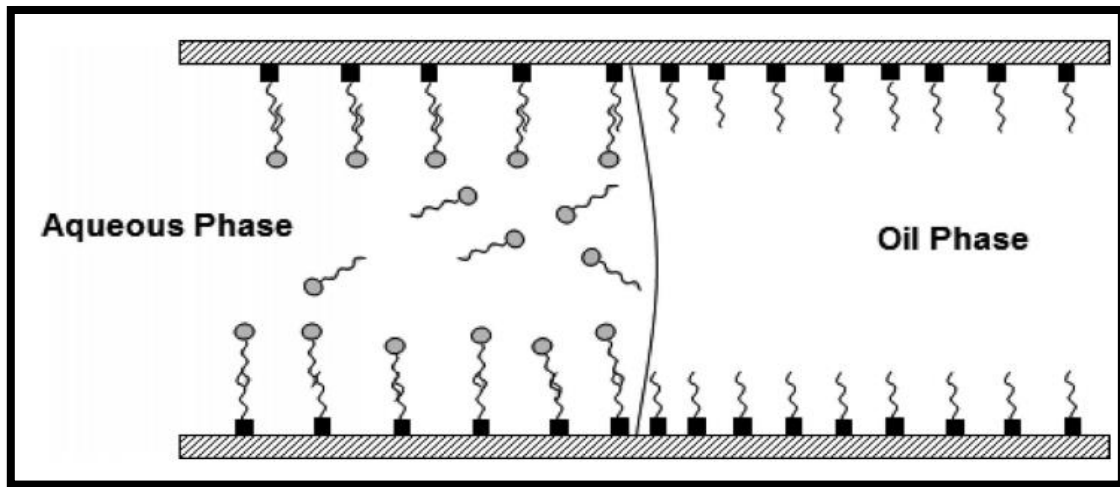


Fig. 7—Schematic diagram showing the process of wettability alteration due to formation of a monolayer of anionic surfactant molecules with the circles being the anionic surfactant molecules and the squares being the adsorbed oleic components (Standnes 2001)

The adsorption isotherm was found to be similar to the Langmuir isotherm which supports the formation of surfactant monolayer on the originally oil-wet rock surface.

Micellar solubilization of adsorbed organic components by anionic surfactants was proposed by Kumar et al. (2005). However, this is seen only at ultra-low IFT since the lipophilic interaction between the carboxylic components in the oil and the anionic surfactant monomers are weak. In order to obtain ultra-low IFT, a large quantity of surfactant was required. Besides, Adibhatla et al. (2005) observed that although increasing surfactant concentration increases the initial rate of recovery, final recovery is insensitive to surfactant concentration. Several different factors such as surfactant structure, temperature and salinity have the potential to affect the degree of wettability alteration and hence, oil recovery by spontaneous imbibition of surfactant enhanced

brine. Anionic surfactants can alter wettability through this mechanism for positively charged carbonate rocks and hence show greater degree of adsorption while cationic surfactants have been suggested to alter wettability in negatively charged sandstone showing larger degree of adsorption (Liu et al. 2003).

2.3.2.2 Wettability Alteration by Ion-Pair Formation

Standnes and Austad (2000) suggested that the accelerated imbibition rates due to cationic surfactant present in the aqueous phase for oil-wet chalk cores resulted from the ability of the surfactant to form ion-pairs between the positive head groups of the cationic surfactant molecules and the negatively charged adsorbed carboxylic groups from crude oil on the surface of the chalk. Electrostatic interactions between the head groups and the stability provided by the lipophilic interactions between the tail sections result in the formation of the ion-pairs. The ion-pairs formed during the process readily move across the oil/water interface into the oil phase as they are not water soluble (Salehi et al. 2008). **Fig. 8** shows the entire process in which the surfactant monomers are suggested to interact and strip the adsorbed oleic compounds off the mineral surface hence strongly altering the wettability of the solid surface to preferential water-wet state. Since these ion-pair interactions are much stronger than the lipophilic interactions that occur due to surfactant adsorption as described in 2.3.2.1, the extent of wettability alteration due to ion-pair interactions is greater than that due to surfactant adsorption alone. This fact possibly explains why cationic surfactants perform better than anionic surfactants in altering wettability of positively charged carbonate rocks to a stronger water-wet state. On the other hand, in the case of oil-wet sandstone rock, anionic

surfactants have shown to be more effective in changing wettability due to the same mechanism. Buckley et al. (1998) demonstrated the affinity of the negatively charged sandstone surface towards the positively charged basic components during the initial process of wettability alteration to oil-wet state by crude oil as described in 2.3.1. Hence, after the aging process, the sandstone surface is covered by an adsorbed layer of positively charged basic oleic components of crude oil. Later, during the wettability alteration process due to surfactants, anionic head groups and positively charged basic components of crude oil originally adsorbed on the sandstone surface form ion-pairs due to the electrostatic interaction between them (Salehi et al. 2008). This results in wettability alteration of sandstone rock surface to a preferential water-wet state due to the introduction of anionic surfactant.

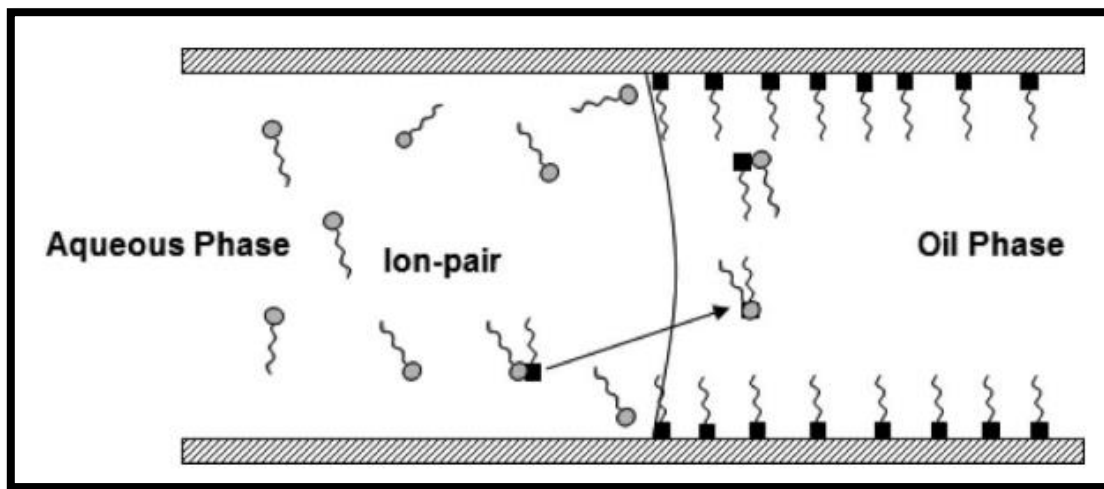


Fig. 8— Schematic diagram showing the process of wettability alteration due to formation of ion-pairs of cationic surfactant molecules in a carbonate solid surface with the circles being the cationic surfactant molecules and the squares being the adsorbed oleic components (Standnes 2001)

2.3 Use of X-Ray Computed Tomography in Surfactant Imbibition Studies

X-Ray computed tomography (CT) is a nondestructive imaging technique that can be used to visualize opaque solid objects like reservoir core samples. The main goal is to attempt to visualize the flow front inside the core during an experiment. A CT image is created due to the difference in radiodensity of objects while passing X-rays through a particular slice plane from multiple orientations. The decrease in the intensity of the reflection of the X-rays from different objects create a particular CT image after complex calculations are performed by specified algorithms to reconstruct the distribution of X-ray attenuation in the slice plane. The biggest advantage of CT methods lies in the fact that it is nondestructive and a core sample can be used multiple times for different experiments allowing greater flexibility while planning a research project.

The X-ray attenuation is represented as gray levels in a CT slice which basically corresponds to the proportion of X-rays scattered or absorbed while passing through each voxel. Voxel (volume element) is a combination of “volumetric” and “pixel” and represents a particular value on a regular grid in a three dimensional space. The X-ray energy and the atomic number and density of the object being visualized determine the attenuation of the X-rays. In a typical CT image of a core, regions of dark and bright voxels can be seen which correspond to areas of low and high radiodensity respectively. Radiodensity refers to the relative inability of the X-rays to pass through a particular material. CT methods have been extensively used in the oil and gas industry since the mid-1980s to study porosity, fluid saturation, and multiphase flow in porous media and

more recently to study surfactant enhanced imbibition in wettability alteration studies and failure mechanisms in triaxial setups (Al-Muntasheri et al. 2010; Alshehri and Kovscek 2012; Babadagli 2001a; Babadagli 2003; Babadagli and Boluk 2004; Bansal and Islam 1991; Bataweel et al. 2011; Chen et al. 2000, 2001; DiCarlo et al. 2000; Galeh-Kalaei et al. 2013; Han et al. 2011; Hasçakır et al. 2011; Hunt et al. 1988; Kalaei et al. 2013; Kalaei et al. 2012; Laboissiere et al. 2013; Nguyen et al. 2003; Seright et al. 2006; Stoll et al. 2007; Weiss and Xie 2007; Withjack et al. 2003; Wong 2003; Xie et al. 2004; Xie et al. 2005; Zhang et al. 2008; Zhang et al. 2009).

During the reconstruction of the CT image, the X-ray attenuation for each voxel is converted into corresponding numerical values defined as CT numbers by normalizing the attenuation coefficient for each voxel with the linear attenuation coefficient of water and air (Akin and Kovscek 2003; Wellington and Vinegar 1988) (Eq. 8).

$$CT = 1, SPE - \times \frac{\mu - \mu_w}{\mu_w} \dots \dots \dots (8)$$

where CT refers to the CT number in dimensionless Hounsfield units (HU) and μ_w is the linear attenuation value for water.

In general, the CT number values for air and water are assumed to be -1SPE- and 0 respectively. Porosity of a core sample can be calculated using CT numbers using Eq. 9 which is based on Beer's law.

$$\varphi = \frac{CT_{wr} - CT_{ar}}{CT_w - CT_a} \dots \dots \dots (9)$$

where the subscripts w and a represent water and air phase respectively, and the subscripts wr and ar refer to water- and air-saturated rock CT numbers, respectively.

Saturation profiles throughout a coreflood experiment can be obtained using CT images. If the system only has two phases, water and oil, in it, the fluid saturations can be calculated using Eqs. 10 and 11.

$$S_o = \frac{CT_{wr} - CT_{wor}}{CT_{wr} - CT_{or}} = \frac{CT_{wr} - CT_{wor}}{\phi \times (CT_w - CT_o)} \dots \dots \dots (10)$$

$$S_o + S_w = 1 \dots \dots \dots (11)$$

where CT_o is the CT number of the oil phase and S_o and S_w are saturation of oil and water respectively.

CT methods can be very effective while studying the potential of surfactants in altering wettability in oil-wet rocks and improving recovery as their implementation allows the visualization of the changing fluid saturations during the experiments.

2.4 Review of Static Imbibition Experiments with Surfactants in Conventional Reservoirs and Low Permeability Shale Reservoirs

2.4.1 Use of Surfactants in Conventional Reservoir Systems

Although this thesis involves work with ultralow permeability oil rich shale reservoirs, it is critical to review the literature on wettability alteration experiments due to surfactants in conventional reservoirs. Three case studies have been presented which discuss surfactant enhanced brine spontaneous imbibition experiments.

2.4.1.1 Schechter et al. (1991)

Schechter et al. (1991) suggested that oil recovery from spontaneous imbibition experiments is driven by a combination of capillary imbibition and gravity-driven flow. In this research work, the effect of reduced IFT on oil recovery by spontaneous imbibition is compared to the effect of gravity segregation for a wide range of IFTs in

vertically oriented cores. Brine concentration was altered to obtain different viscosity ratios in this work. The researchers concluded that there is a crossover from capillary to gravity-driven imbibition based on the permeability of the core. For high permeability sandstone cores, gravity forces acted as the dominant recovery mechanism while for low permeability limestone cores, capillary forces were responsible for the oil recovery. These conclusions resulted in the researchers arriving at the inverse bond number discussed earlier.

2.4.1.2 Austad and Milter (1997)

Austad and Milter (1997) used surfactants to improve spontaneous imbibition of water into oil-wet low permeability (2-3 md) chalk cores. Cores of varying length and different wettability i.e. water-wet, oil-wet, and intermediate-wet were used for these experiments. Both anionic and cationic surfactants providing IFT values of 0.02 mN/m and 1 mN/m were used in these experiments. The researchers observed that for the water-wet and mixed-wet cores, there was significant oil production even without any surfactant. They suspected that the oil production was governed by strong capillary forces which were further bolstered by the Maragoni effect. The use of surfactant in these types of cores reduces the IFT and resulted in very low rates of imbibition. One clear conclusion that was provided by this research was the fact that existence of capillary forces was essential for oil recovery in static imbibition test since without any capillary forces and significant diffusion or gravity forces, transport of surfactant enhanced brine into the rock matrix would not be possible.

2.4.1.3 Adibhatla and Mohanty (2008)

Adibhatla and Mohanty (2008) worked on the viability of numerically modeling surfactant enhanced imbibition in oil-wet carbonate rocks. In this work, a three dimensional, finite-volume, two-phase, multi-component, fully implicit numerical simulator was developed which captured the effects of adsorption, wettability alteration, and phase behavior, among others. The numerical simulation study was finely calibrated with the results from their core scale spontaneous surfactant imbibition experiments conducted in their lab. The primary conclusion of this simulation study discusses the impact of IFT on recovery rate. The researchers suggested that in the occasion when surfactant alters the wettability of the rock, higher recovery rates are observed for higher IFTs and when the surfactant does not alter the wettability of the rock, lower IFTs give higher recovery. These conclusions are clearly in line with the discussion about capillary pressures in 2.2.3.3. Lowered IFT reduces the capillary forces in the system and that lowers the oil recovery as shown by this study.

2.4.1 Use of Surfactants in Unconventional Reservoir Systems

Although several other similar studies on wettability alteration by surfactants in conventional reservoirs have been conducted and explained in the literature, it does little when the discussion shifts to nanodarcy permeability oil rich shale reservoirs. At this point of time, very limited literature is available for wettability alteration in shale reservoirs in general. One particular study is discussed in this section.

2.4.1.1 Wang et al. (2012)

Wang et al. (2012) published their work on wettability survey in Bakken shale using surfactant formulation imbibition. They found that wettability in the Bakken shale can be modified by several complex interactions based on the pH, temperature, or surfactant access to the matrix rock. The wettability of different parts of the Bakken formation was determined in order to investigate the potential of surfactant formulations that can imbibe into the shale matrix and improve oil recovery.

A modified version of the standard Amott-Harvey test discussed in 2.2.1.2 was used to determine wettability of cores obtained from three different wells at different portions of the Bakken formation. The Bakken shale cores were found to be generally oil-wet or intermediate-wet. After performing surfactant imbibition tests on both clean and unclean shale core samples, it was concluded that imbibition of surfactant formulations had a substantial potential to improve oil recovery from the Bakken formation. Incremental recoveries in experiments with surfactant formulations over brine only ranged from 6.8% to 10.15% OOIP.

The conclusions reached by Wang et al. are favorable towards the investigation outlined in this thesis since the primary objective of this research work is also to analyze the potential of surfactants in altering wettability in ultra-tight oil rich shales and improving oil recovery. However, there is a key difference between this study and the study conducted by Wang et al. in the fact that the shale core samples used in the experiments by Wang et al. had permeability of around 40 microdarcies while the reservoir being investigated in this study have much lower permeability in the nanodarcy

range. There has not been any published literature which discusses oil recovery improvement by wettability alteration in nanodarcy oil shale reservoirs making this investigation and thesis first of its kind.

2.5 Numerical Modeling of Wettability Alteration by Surfactants

Reservoir simulation has been successfully used in the industry to study reservoir performance under different scenarios. Special processes like surfactant flooding can also be investigated using reservoir simulators to model and forecast improved reservoir performance, if any. Most commercial simulators offer a surfactant processes plugin which can be used to understand the effect of surfactants on wettability and oil recovery. Schlumberger's ECLIPSE E100 with an active surfactant module was used to model the lab experiments and further upscale it to the field scale simulations. This section describes the steps used by ECLIPSE to capture the process of wettability alteration that occurs during surfactant imbibition experiments.

The wettability alteration model in ECLIPSE works by interpolating relative permeability curves and capillary pressures between two extreme states of wettability, i.e. strongly water-wet and strongly oil-wet. The relative permeability and capillary pressure for each block are calculated using a linear interpolation between relative permeability curves and capillary pressure curves of the initial and final wetting states as shown in Eq. 12. The weighing factor Ψ is based on the concentration of surfactant adsorbed in that particular grid block as shown in Eq. 13.

$$k_r = \Psi k_r^{water-wet} + (1 - \Psi) k_r^{oil-wet} \dots \dots \dots (12)$$

$$\Psi = \frac{C_{surf.adsorbed}}{C_{surf.adsorbed} + C_{surf.total}} \dots \dots \dots (13)$$

where the superscripts denote the wetting state of the relative permeability table and $C_{surf.adsorbed}$ and $C_{surf.total}$ are the adsorbed and total surfactant concentration in each grid block respectively.

The capillary pressure of each grid block is also treated in the same manner to account for the alteration of wettability in the grid block. Although the weighing factor is defined to depend on the adsorbed and total surfactant concentration, a constant value has been typically used in similar studies (Delshad et al. 2006). The weighing factor can also be treated as a history matching parameter and altered until a good match between the observed and simulated data is obtained.

3. BACKGROUND INFORMATION

This section provides background information about the different aspects of the project in detail. Since this project was dictated by an underlying confidentiality agreement between Texas A&M University and a large independent operator which funded this research work in its entirety, absolute information about the chemicals or field being studied cannot be disclosed in this thesis. However, the discussion of the characteristic properties of the field and the chemicals involved is permissible without divulging absolute information.

3.1 Reservoir Description

Numerous shale plays have become profitable ventures for operators to develop with immense technological progress in stimulation techniques and well design as discussed in Section 1. The shale play investigated in this research would be referred to as Shale A throughout this thesis. Shale A is one of the newest shale plays to have joined the league of other prolific plays like Bakken, Eagleford and Woodford. This research work involves cores extracted from wells in this play.

The operator which funded this research would be referred to as Company X throughout this thesis holds the largest acreage in this shale play. This formation lies underneath a naturally fractured field which until recently was the sole target for reservoir development for the operator. The operator holds a legacy position in the naturally fractured field with over 900, SPE- gross acres and a current producing well count over 7 SPE- vertical wells. Recently, the operator chose to drill deeper beyond the

conventional formations targeting the Shale A formation by implementing horizontal well technology and this resulted in a number of tremendous wells.

Shale A is a prolific play with average thickness of up to 1750 ft in the central part of the Midland Basin. The play is subdivided into four major intervals referred to here as Zone L, M, N, and O. There is significant variability among the intervals although organic matter is observed across all the intervals and the composition of all the intervals is principally “shale”. Company X has reported Zones L, N, and O as the intervals which show economic rates and EURs, with Zone M being the best out of the three. Zone L is carbonate rich, while Zone M contains more quartz than carbonate, along with a higher organic content. The N member shows the highest thickness with significant clay content. Multiple para-sequence boundaries which can be correlated across huge parts of the basin are encompassed in the O interval. The magnitude of potential hydrocarbon reserves in this shale formation is so enormous that it is extremely important to adopt a development strategy that can optimize EURs. Since the performance of an unconventional shale well depends on the performance of the stimulation job to a great extent, optimizing the stimulation job is the key to optimizing EURs of wells in the Shale A play. The motivation behind this research work entirely lies in this very fact.

3.2 Core Description

Core plugs and trims of two Shale A wells—Well A and Well B, were used in this research work. The core plugs and trims were received from a core testing laboratory and were not in a preserved state. The process of core preparation and aging

will be discussed in a later section. A total of 58 samples were available for Well A ranging from a depth of 8,335.50 ft to 8,434.10 ft while 60 samples were provided for Well B with depths ranging from 7,791.95 ft to 7,910.20 ft. Several core plugs and trims from various depths were selected for both wells to conduct the experiments. The trims were used for the contact angle measurements while the whole plugs were used for the spontaneous imbibition experiments in the CT scanner. **Fig. 9** shows a sample core plug and trim that were used for the spontaneous imbibition and contact angle experiments.



Fig. 9—Sample plug and trim used in the experiments

3.3 X-Ray Diffraction (XRD) Analysis

XRD analysis was conducted prior to the start of the experiments in order to understand the major mineral composition of the core samples. **Fig.10** shows a sample

XRD pattern for a representative Shale A sample. The major minerals in the shale comprise of quartz, feldspar, dolomite, calcite, pyrite and other trace silicate clay minerals. The red ellipse highlights the XRD response from these silicate clays which is dwarfed by the response of the major minerals. Special clay separation was performed to identify the clay minerals. Illite, smectite, and mica were the major clay minerals in the shale sample.

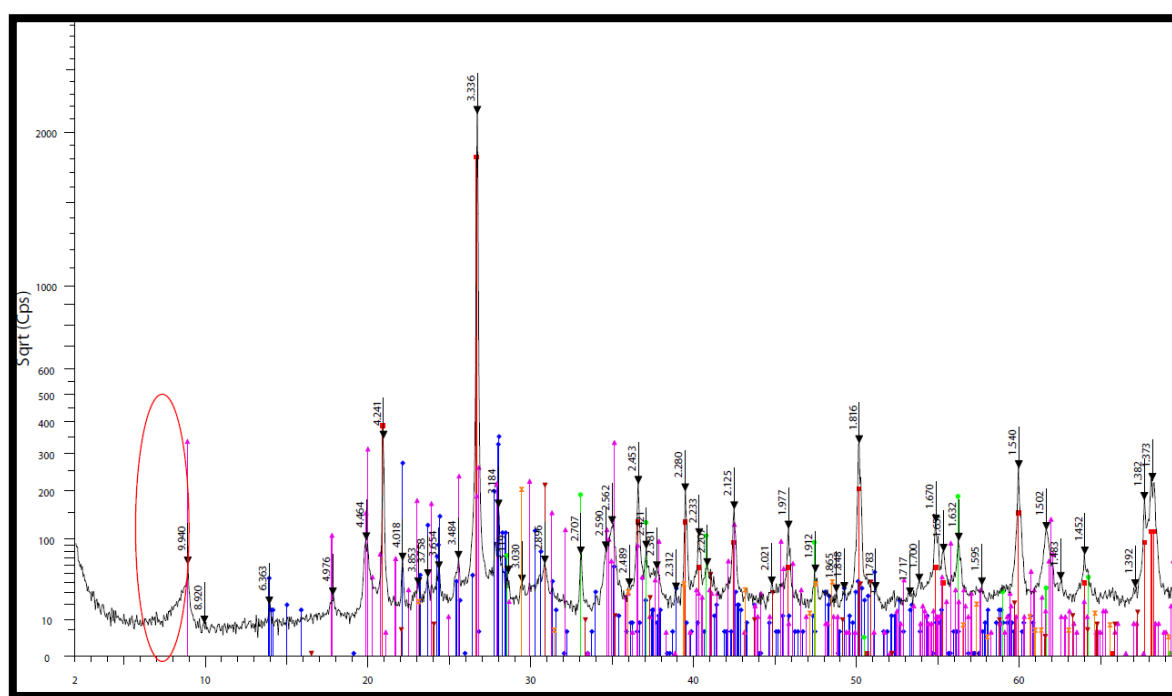


Fig. 10—XRD pattern of a Shale A core sample

The information about mineralogy is important since the successful implementation of wettability alteration by surfactant depends on the composition of the rock to a great extent as discussed in Section 2. The Shale A formation is tricky because

it contains both quartz and carbonate in varying proportions across the formation. **Table 1** shows a comparison of the major minerals from three different depths obtained from XRD analysis. Sample 1 contains more quartz than carbonate while samples 2 and 3 clearly show the presence of both quartz and carbonate minerals. Illite is the major clay in samples 1 and 2 while mica content is higher in sample 3.

Table 1—XRD analysis comparison for different Shale A depths

Sample #	1	2	3
Depth	7791.95	7828.1	7910.2
Mineral Weight %			
Quartz	40.3	13.1	8.2
Feldspar	6.5	3.5	1.2
Calcite	2.3	46.2	15.3
Dolomite	1.7	19.6	64.2
Pyrite	8.9	2.5	0.7
Total Clays	40.3	15.1	10.4
Relative Clay %			
Illite	63.2	54.2	25.9
Smectite	4.5	5.7	0.5
Mica	32.3	40.1	73.6

As previously discussed, anionic and cationic surfactants have the potential to alter wettability in quartz and carbonate formations respectively by the mechanism of ion-pair formation. However, in the case of mixed mineralogy formation like Shale A,

the application of ion-pair formation mechanism becomes tricky. In such formations, the use of non-ionic surfactants can be tested as it alters wettability in rock by forming a monolayer due to hydrophobic interactions and not by ion-pair formation. In summary, the XRD analysis provided a good starting point for this research work as it indicated the types of surfactants that can potentially alter wettability in this formation.

3.4 Description of Shale A Crude Oil

Shale A crude oil, courtesy Company X, was used in all the experiments. The reservoir temperature is known to be around 165° F. The density and viscosity of the crude oil at 165° F was measured as 0.79 g/cc and 2.11 cp respectively. **Fig. 11** shows a sample of the crude oil used in the experiments.

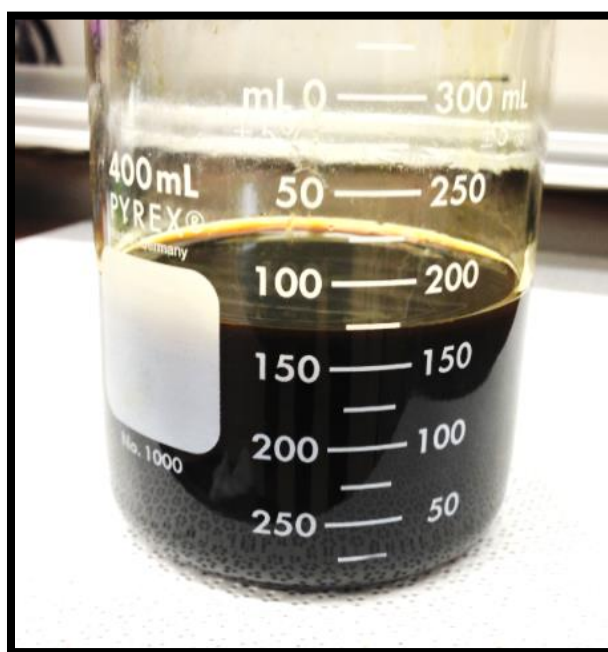


Fig. 11—Shale A crude oil sample

3.5 Description of Surfactants and Other Stimulation Fluid Components

The surfactants tested in this research work along with the other components of the stimulation fluids were provided by Company X. The stimulation fluid comprised of typical components like brine, a gel slurry, clay stabilizer, crosslinker, biocide and surfactant. A total of five different surfactants were tested. **Table 2** lists the surfactants used in this research work.

Table 2—Description of the surfactants used in the experiments

Surfactant Name	Type	Primary Component	pH	Relative Density
Surf A	Nonionic	Branched alcohol oxyalkylate	5.0-7.0	0.99-1.03
Surf B	Nonionic	Ethoxylated isodecylalcohol	7.0-9.0	1.02-1.05
Comp A	Complex Nanofluid	Proprietary Citrus Terpenes	6.8-8.3	0.95-0.96
Comp B	Complex Nanofluid	Proprietary Citrus Terpenes	4.0-7.0	0.90-0.96
Comp C	Complex Nanofluid	Proprietary Citrus Terpenes	5.0-8.0	0.96-1.01

Surf A and Surf B are traditional nonionic surfactants containing branched alcohol oxyalkylate and ethoxylated isodecylalcohol compounds respectively whereas Comp A, B, and C belong to a novel category of “surfactants” called complex nano-surfactant. These fluids containing nano sized particles cannot be classified using the typical surfactant classification as they act more like a “micro-emulsion” in the nano scale. The main components of Comp A, B, and C are proprietary and hence, the

composition of these three chemicals was unknown during the course of this research work.

Fig. 12 shows the surfactants and the other stimulation fluid components that were used in the experiments. The names of the chemicals have been blocked due to confidentiality issues.



Fig. 12—Surfactants and other stimulation fluid components used during this research work

In summary, this research work involved the comparison of traditional surfactants with a new range of surfactants which are gaining extreme popularity in the industry. There is a big cost difference between the traditional surfactants and the novel complex nano surfactants and hence, it was interesting to see whether the performance of this new range of surfactants in altering wettability and improving oil recovery is worth the additional price and the hype.

4. CONTACT ANGLE MEASUREMENT EXPERIMENTS

This section describes the contact angle experiments that were conducted to determine the wettability of the shale samples. As discussed in section 2, contact angle measurement is one of the three techniques which can determine the wettability of a matrix. The Amott-Harvey and the USBM methods are used to determine the average wettability of a specific volume such as a core and cannot determine the wettability of a surface. Since the Shale A cores are extremely tight with ultralow permeability, wettability determination using the Amott-Harvey or the USBM method is difficult. Contact angle measurement is the most efficient and practical method to determine the wettability of the shale core samples, especially when several samples need to be tested within a limited timeframe.

4.1 Sample Preparation and Aging Process

The samples for the contact angle experiments were derived from the end trims and failed plug in order to preserve the plugs for the imbibition experiments. The end trims and failed plugs were precisely cut and polished into 1 cm x 1 cm x 0.3 cm chips. The dimensions of the chip had to be precise since anything larger would not fit in the contact angle measuring device. **Fig. 13** shows a sample shale chip used for the contact angle measurement experiments. A few of the samples were cleaned while the others were left as received. The cleaning process involved soaking the chips first in toluene and then in methanol and finally air drying them. The cleaning process was performed in

order to determine whether cleaning impacted the wettability results and if it is essential.

Fig. 14 shows the comparison of a clean and an unclean shale chip.

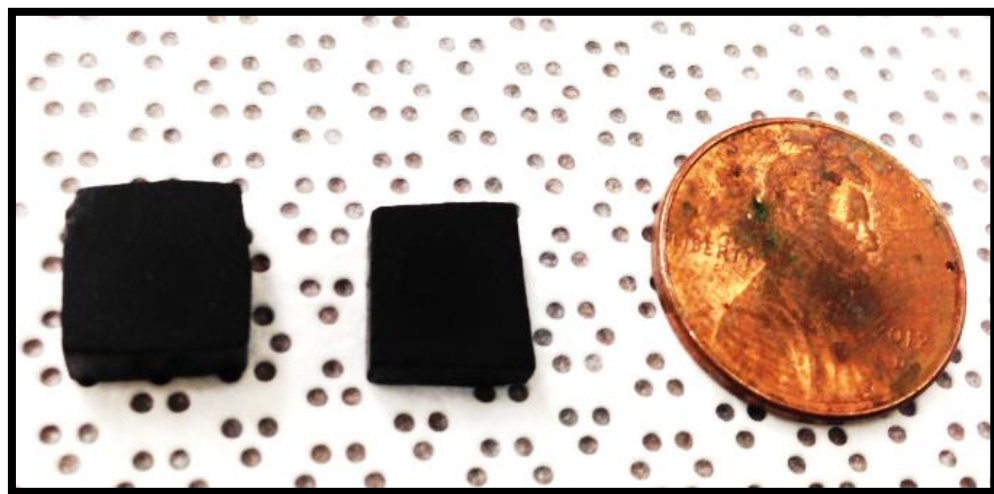


Fig. 13—Shale A chip samples used for contact angle measurements

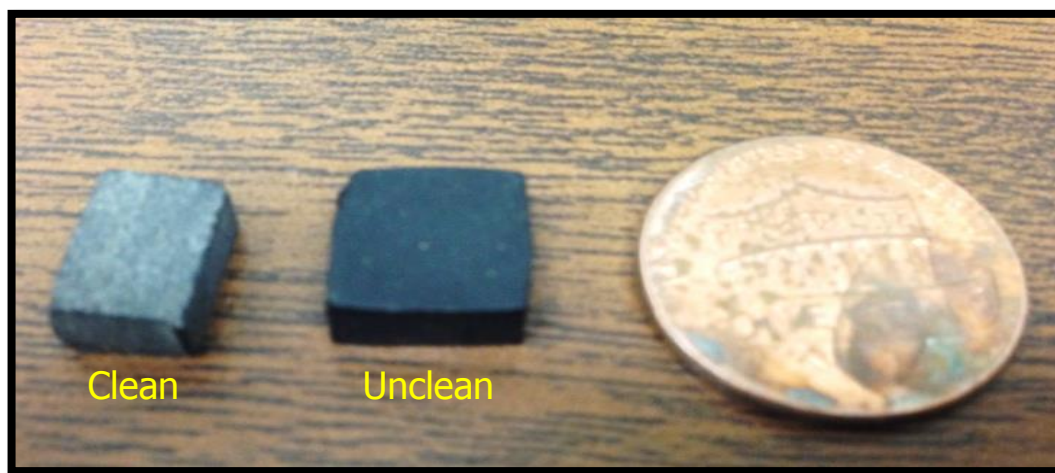


Fig. 14—Clean vs. unclean shale chip samples

After the preparation of the samples, the samples were put in beakers containing Shale A oil and allowed to age at the reservoir temperature of 165 °F for over four months.

4.2 Experimental Method and Setup

The main objective of the contact angle experiments was to determine the wettability of the Shale A core samples and investigate the potential of surfactant enhanced brines to alter wettability of the matrix. A simple approach toward contact angle measurements could be to just measure the contact angle of one fluid on the matrix in the presence of air. **Fig. 15** shows a visual comparison of the contact angles formed by three different fluids on a shale surface. However, the interaction between the fluids and the surface can dramatically change when another fluid replaces air as the second fluid. In such a case, the measured contact angles can be very different than those obtained while air acted as the second fluid in the system.

In order to correctly investigate the potential of surfactants in altering wettability in shales, it is important that an accurate representation of the reservoir system is made during the contact angle measurements. In a typical reservoir system, the two fluids which attempt to wet the rock surface are the oil/ hydrocarbon liquid and the brine. Therefore, in order to accurately determine wettability, the contact angle of one fluid in the presence of the other is required. Since, it is not possible to see through crude oil, the contact angle of a droplet of brine on the shale surface in presence of oil is not possible. Hence, the contact angle of an oil droplet in presence of brine provides the closest representation of the system's wettability.

Although contact angles can be measured using several methods such as the sessile drop, captive bubble, tilting plate, and capillary rise, among others, the sessile drop and the captive bubble method are the most widely employed methods as they provide easily accessible and reproducible contact angles (Montes Ruiz-Cabello et al. 2011). The captive bubble method was used in this research work as it allows accurate measurement of contact angle of an oil droplet on a shale surface in presence of brine. A Dataphysics OCA 15 Pro device was used for the captive bubble measurements as shown in **Fig. 16**. Apart from static and dynamic contact angles, this device can also measure surface tension, IFT, and surface free energy of solids. A temperature control unit made it possible to maintain the reservoir temperature of 165 ° F.

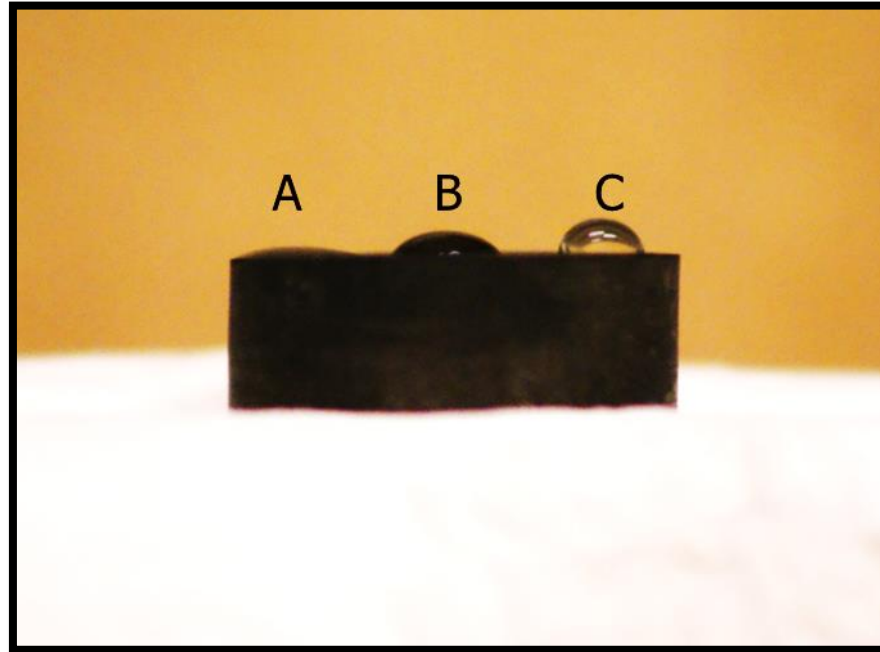


Fig. 15—Comparison of the contact angles for three different fluids

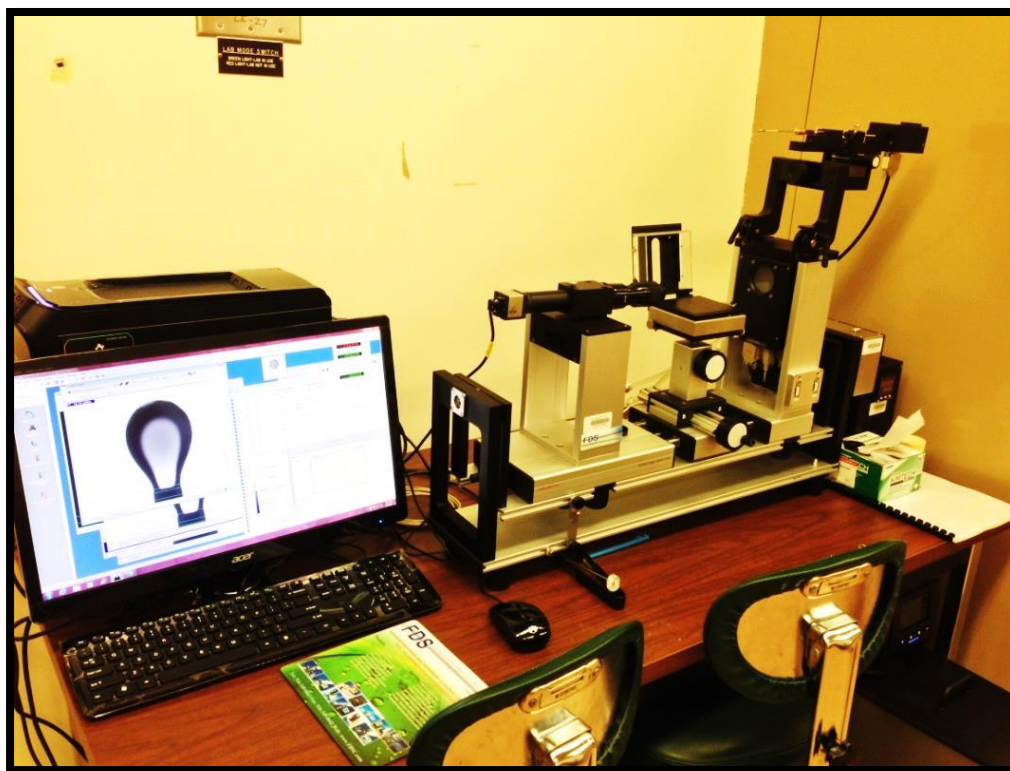


Fig. 16—Contact angle measuring device

4.2.1 Experimental Setup

In the captive bubble method, a J-shaped capillary needle dispenses a droplet of oil on the bottom of a sample surface in the presence of brine contained in a cuvette. **Fig. 17** provides a schematic of the process. The aged shale sample is put in a cuvette while contains the simulation fluid. A syringe containing Shale A oil is connected to a J-shaped capillary needle which dispensed an oil droplet on the bottom surface of the shale sample. A high resolution camera captures this entire process and sends the data to the compute where the images are analyzed and the contact angles calculated. **Fig. 18** shows a picture of the actual experiment in progress.

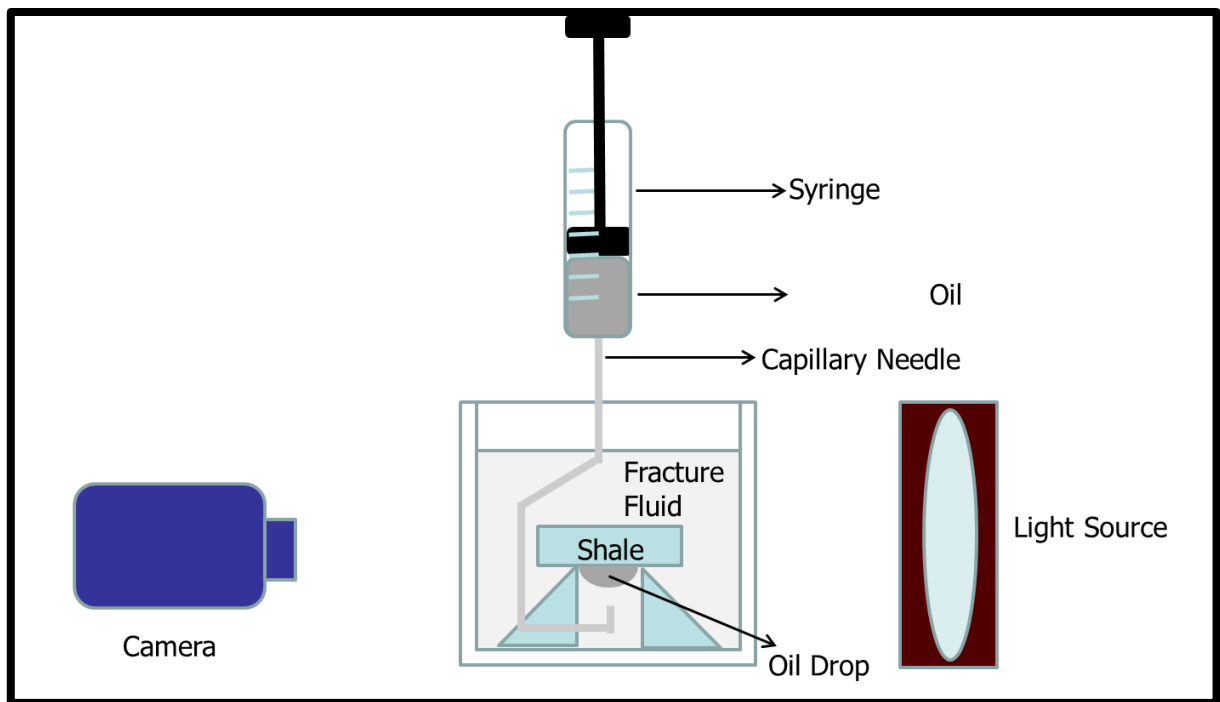


Fig. 17—Contact angle measurement using the captive bubble method where the oil droplet is dispensed on the bottom surface of the shale sample

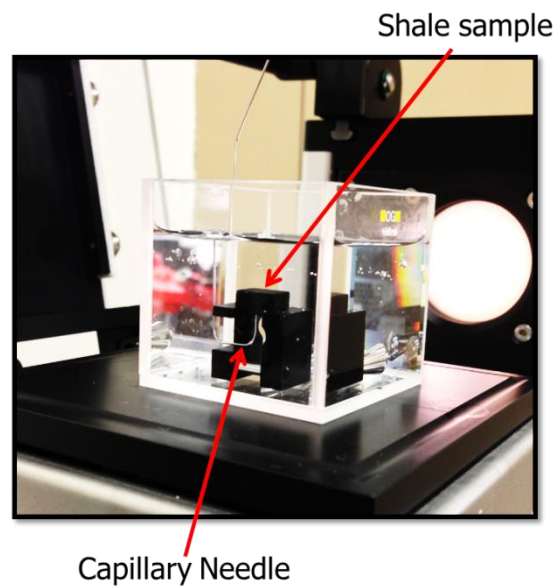


Fig. 18—Contact angle measurement using captive bubble method

4.2.2 Experimental Design

The contact angle measurements were performed for stimulation fluid without any surfactant (frac water) and stimulation fluid enhanced with each of the five surfactants individually. The surfactants were tested for three different concentrations of 0.2 gallons per thousand gallons (gpt), 1 gpt, and 2 gpt. 1 gpt is equivalent to 1SPE-parts per million (ppm). In order to maintain clarity in the stimulation fluid which is required for contact angle measurements using an optical device like the one used in his research work, only surfactant, biocide and clay stabilizer were added to the frac fluid. The gel slurry and crosslinker were not used during the contact angle measurements.

Shale chip samples from three different depths of Well A and B were used for the experiments. To achieve repeatability and consistency, 5-6 trials for each core depth for a particular surfactant at a specific concentration were performed. Both clean and unclean samples were tested as referenced in section 4.1 to study the impact of the cleaning process.

4.3 Results and Discussion

Before investigating the potential of surfactants, the native wettability of the shale samples was determined. The average contact angle without any surfactant for the three core depths was measured as 110.1° . The general convention used for reporting contact angles is with reference to water i.e. contact angle of a water droplet on a rock surface in the presence of oil. Since the contact angle of an oil droplet on the shale surface in presence of water was measured in these experiments instead, the contact angles reported were in reference to the oil droplet and hence, had to be subtracted from

180 ° to obtain the generally reported contact angle with respect to water. All contact angles reported in this thesis are with respect to water.

A contact angle of 110.1° clearly suggests that Shale A demonstrates a state of intermediate wetness. The next step was to measure the alteration of wettability due to the addition of surfactants to the stimulation (fracture) fluid. **Table 3** shows the contact angle results for surfactants at a concentration of 0.2 gpt. Addition of any surfactant showed a decrease in contact angle. The nano-surfactants, Comp A, B, and C showed to reduce the contact angle better as compared to the traditional nonionic surfactants, Surf A and B. Surf A performed the worst while Comp A was the best as far as lowering the contact angle is concerned. According to the classification of wettability discussed in section 2.2.2, only Comp A was barely able to reduce the contact angle to a state which could be considered as water-wet ($\theta < 75^\circ$). One preliminary conclusion that could be reached from these results is the fact that a surfactant concentration of 0.2 gpt is too low regardless of the surfactant type for this COBR system to achieve any wettability alteration. **Fig. 19** shows the reduction in contact angle observed as compared to frac water alone due to the addition of surfactant to the brine. **Fig. 20** shows sample captured images for experiments at surfactant concentration of 0.2 gpt which are used by the device to compute the contact angles.

Table 3—Contact angle results for surfactants at 0.2 gpt

Core Sample #	Frac Water	Surf A	Surf B	Comp B	Comp C	Comp A
Core Sample Depth 1	109.95	91.2	82.4	78.4	79.2	74.7
Core Sample Depth 2	107.65	90.6	83.3	80.3	78.2	73.1
Core Sample Depth 3	112.75	93.6	87.7	83.9	83.6	75.7
Mean Contact Angle	110.1	91.8	84.5	80.8	80.3	74.5

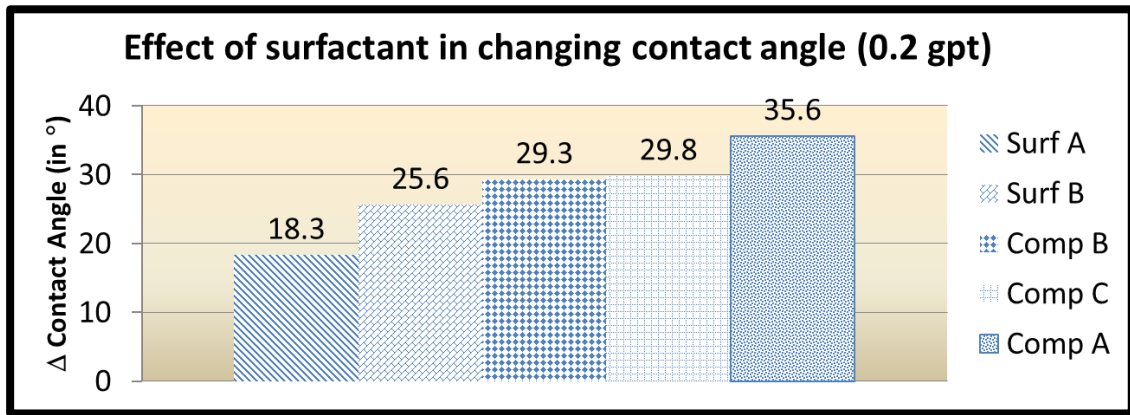


Fig. 19—Reduction in contact angle due to addition of 0.2 gpt surfactant to brine

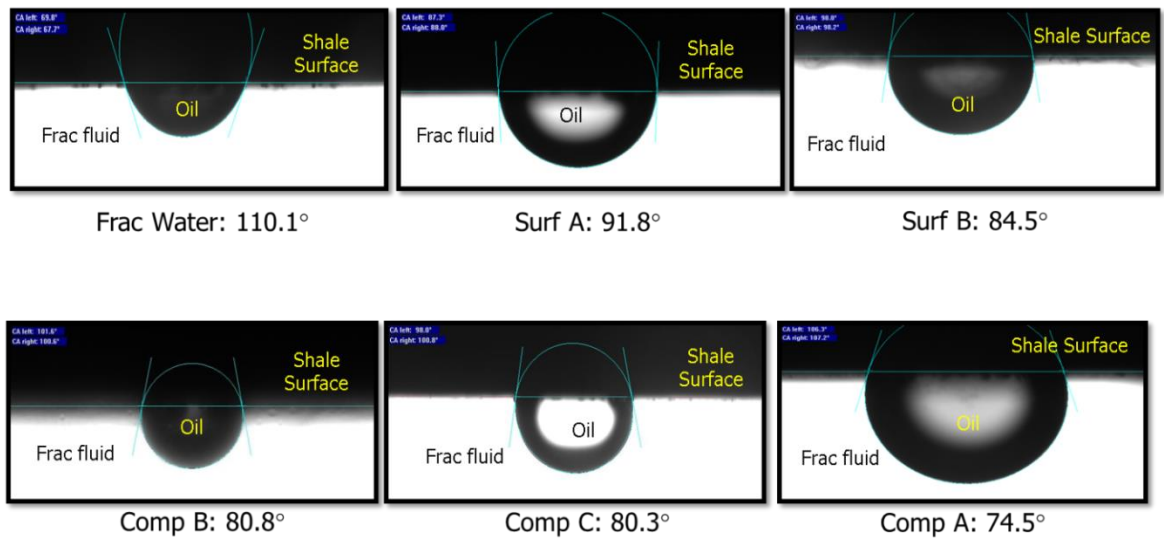


Fig. 20—Change in the oil droplet shape due to the addition of 0.2 gpt surfactant

The next set of experiments was conducted for the surfactants with a concentration of 1 gpt. **Table 4** summarizes the contact angle results for surfactants at 1.0 gpt concentration. The increase in concentration of surfactant resulted in a greater decrease in contact angle across all surfactants. According to the classification of wettability in section 2.2.2, all surfactants but Surf A were able to alter the wettability of the shale surface to preferentially water-wet state. Comp A was the most effective surfactant in lowering the contact angle of the COBR system, followed by Comp B, Comp C, Surf B, and Surf A.

Table 4—Contact angle results for surfactants at 1.0 gpt

Core Sample #	Frac Water	Surf A	Surf B	Comp B	Comp C	Comp A
Core Sample Depth 1	109.95	79.7	70.7	62.1	61.3	61.4
Core Sample Depth 2	107.65	80.8	65.6	61.8	65.3	57.7
Core Sample Depth 3	112.75	78.8	68.79	58.8	66.7	58.9
Mean Contact Angle	110.1	79.8	68.4	60.9	64.4	59.3

Fig. 21 shows the relative change in contact angles as compared to frac water alone due to addition of surfactant at 1.0 gpt concentration. The effect of surfactants in lowering the contact angle is comparable for the complex nano-surfactants. However, between the traditional nonionic surfactants, Surf B performs much better than Surf A in altering the wettability of the system. **Fig. 22** shows sample captured images for experiments at surfactant concentration of 1.0 gpt that are used by the device to compute the contact angles.

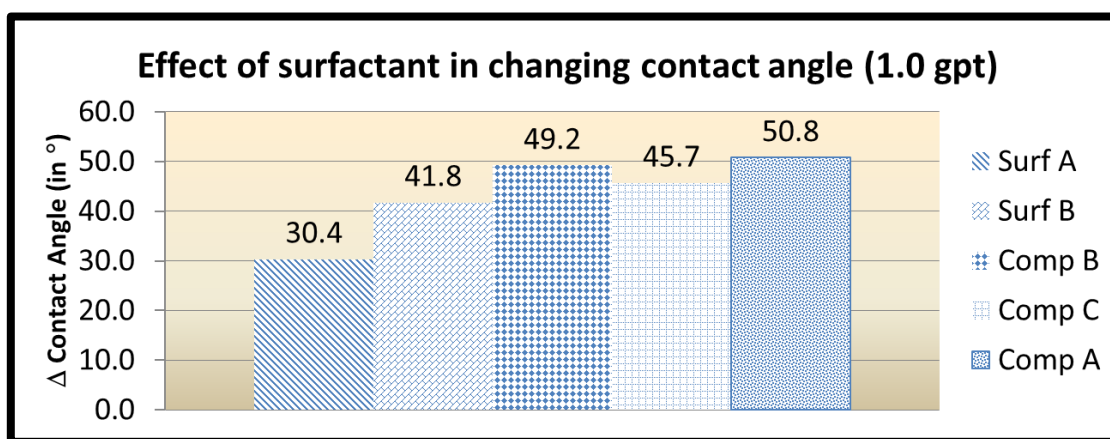


Fig. 21— Reduction in contact angle due to addition of 1.0 gpt surfactant to brine

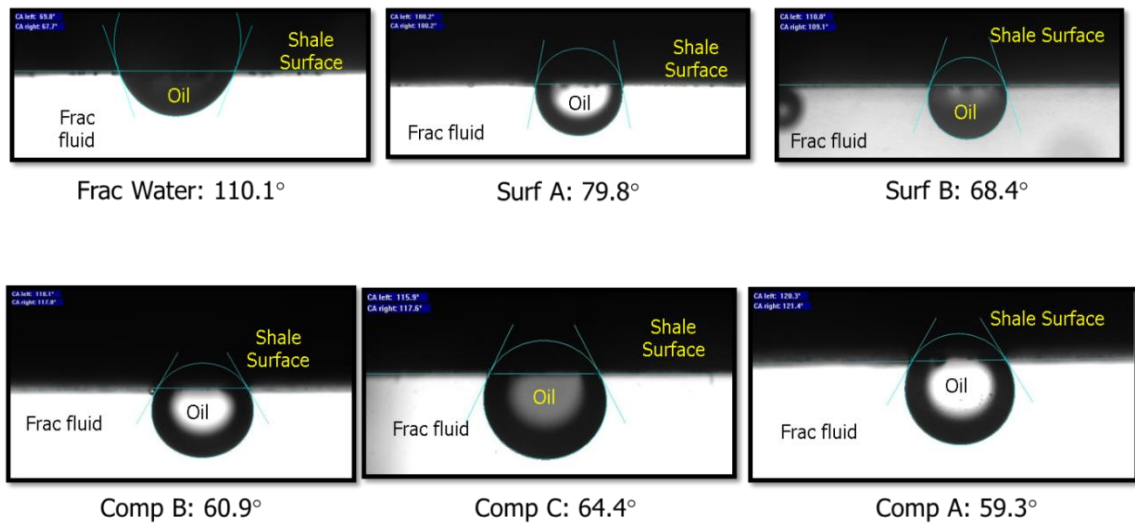


Fig. 22— Change in the oil droplet shape due to the addition of 1.0 gpt surfactant

The last set of experiments was to investigate the potential of surfactants in lowering contact angle at 2.0 gpt concentration. **Table 5** summarizes the contact angle results for 2.0 gpt surfactant concentration.

Table 5— Contact angle results for surfactants at 2.0 gpt

Core Sample #	Frac Water	Surf A	Surf B	Comp B	Comp C	Comp A
Core Sample Depth 1	109.95	74	47.9	38.1	47.3	35.4
Core Sample Depth 2	107.65	70.2	47.4	36.6	47.1	34.1
Core Sample Depth 3	112.75	72.3	49.6	39.3	45.3	36.3
Mean Contact Angle	110.1	72.2	48.3	38	46.6	35.3

Increasing the surfactant concentration to 2.0 gpt improves the performance in lowering contact angle across all surfactants significantly. At this concentration, every surfactant can be considered to have the potential of altering the wettability of the

system to a water-wet state. All surfactants except Surf A, actually alter the wettability of the system to a strongly water-wet state ($\theta < 50^\circ$) at this concentration.

Fig. 23 shows the relative change in contact angles as compared to frac water alone due to addition of surfactant at 2.0 gpt concentration. The performance of Surf A in lowering contact angle was much worse than the four other surfactants. At 2.0 gpt concentration, the performance of Surf B stands out since it proves to be just as effective as Comp C in lowering contact angle and altering wettability. At this concentration, Comp A and Comp B show comparable performance in altering wettability. **Fig. 24** shows sample captured images for experiments at surfactant concentration of 2.0 gpt that are used by the device to compute the contact angles.

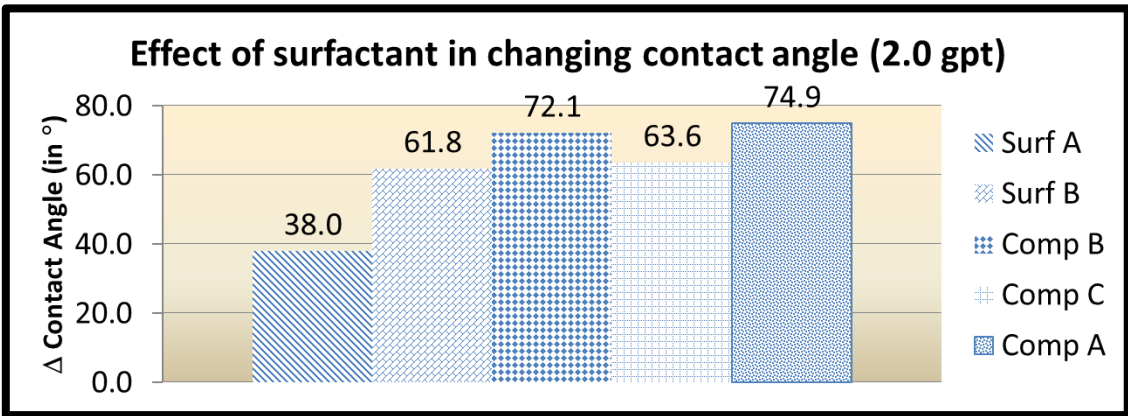


Fig. 23— Reduction in contact angle due to addition of 2.0 gpt surfactant to brine

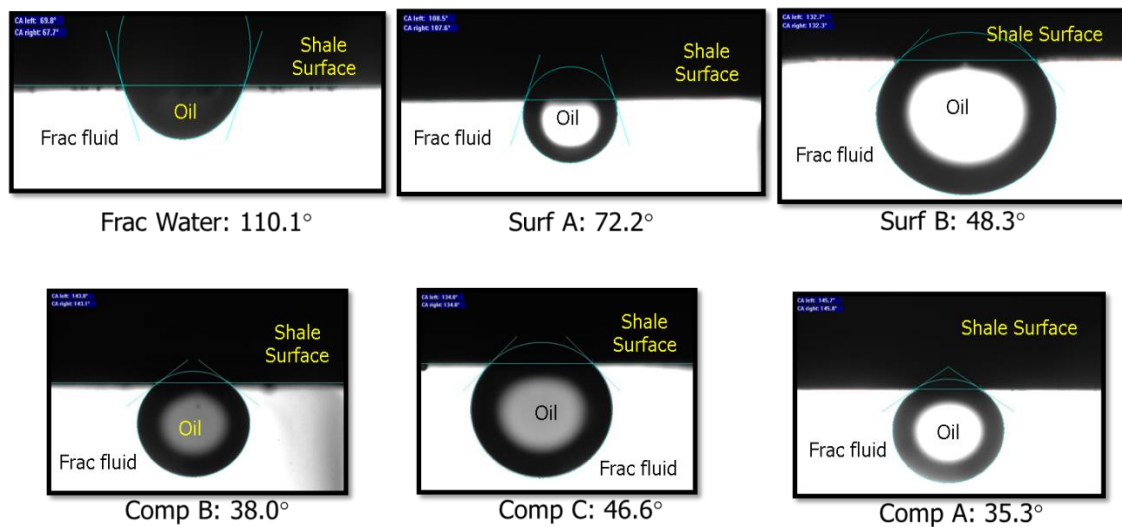


Fig. 24— Change in the oil droplet shape due to the addition of 2.0 gpt surfactant

The contact angle experiments demonstrate the ability of the surfactants to alter the wettability of the Shale A COBR system. In summary, the native wettability of the Shale A formation can be considered as intermediate-wet with a contact angle of around 110°. Each of the five surfactants possesses the potential of lowering the contact angle in varying degree. **Fig. 25** shows a summary of the results of the contact angle experiments. At a concentration of 0.2 gpt, all surfactants but Comp A, fail to alter the wettability of the system from intermediate-wet to water-wet. Comp A lowers the contact angle enough to barely reach an altered state of wettability. It is safe to conclude here that a concentration of 0.2 gpt is too low for any surfactant to achieve any significant wettability alteration.

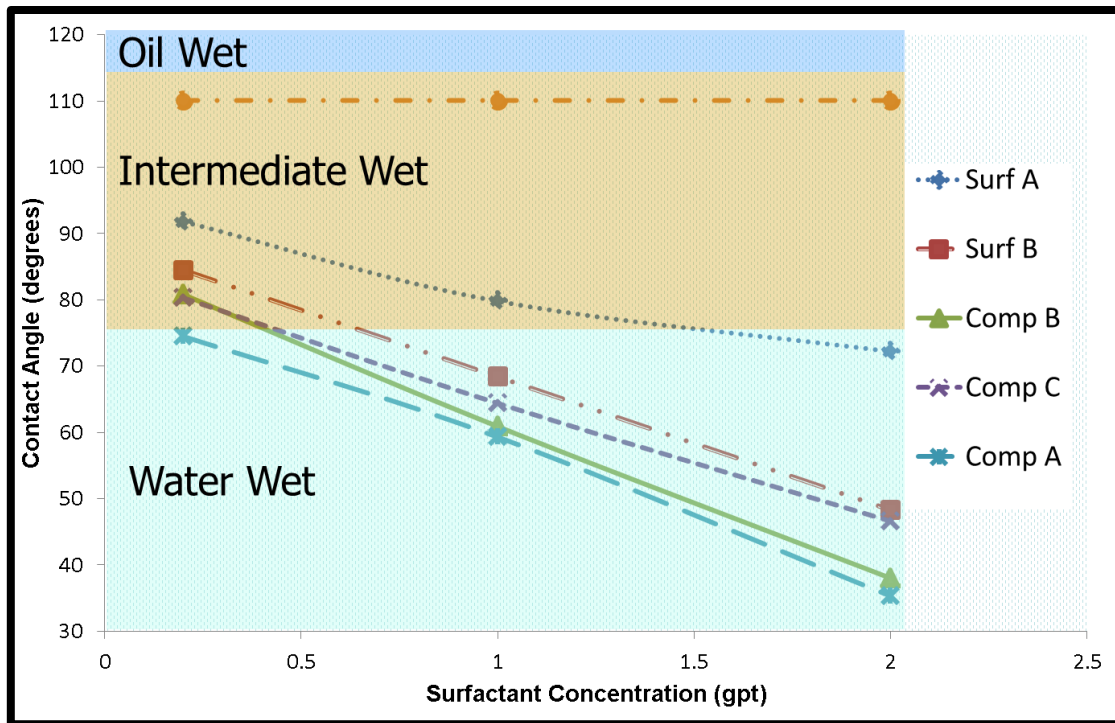


Fig. 25—Summary of surfactant potential in altering wettability in Shale A COBR system

At a concentration of 1.0 gpt, all surfactants but Surf A alter the wettability to a water-wet state. Surf A requires the highest tested concentration of 2.0 gpt to alter the wettability of the system to a water-wet state. At this concentration, the four other surfactants lower the contact angle significantly for the COBR system to be considered at a strongly water-wet state. The cleaning of the samples did not make any difference in the contact angle results. After aging in the crude oil, the results for clean and unclean samples were very similar.

In general, the performances of the three complex nano-surfactants are comparable to each other while there is a big difference in the performances of the two

nonionic surfactants. **Fig. 26** shows the ability of the surfactants to alter wettability in this shale formation relative to each other.

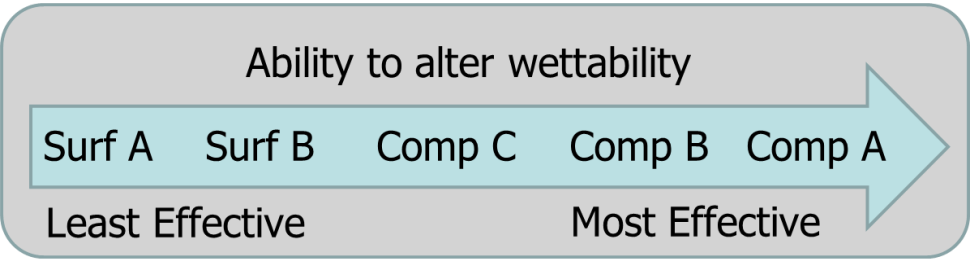


Fig. 26—Comparison of the ability of surfactants to alter wettability in shale

Surf B performs significantly better than Surf A regardless of the concentration used. At this stage of research, it was almost evident from the contact angle results alone, that Surf A cannot compete with the four other surfactants as far as wettability alteration is concerned. The impressive performance of Surf B in altering wettability stands out in these contact angle experiments. Being a traditional nonionic surfactant, Surf B costs much lesser than the three complex nano-surfactants, and if the wettability alteration performance shown in the contact angle experiments translates to improved oil recovery performance, Surf B could be the most cost effective surfactant to improve oil recovery in the Shale A formation.

5. INTERFACIAL TENSION MEASUREMENT EXPERIMENTS

Section 4 investigated the potential of surfactants in altering wettability of the Shale A COBR system. Wettability is only one of the two important factors that determine the magnitude of the capillary forces. IFT along with the wettability of the system determine the effectiveness of capillary forces in improving oil recovery by the process of imbibition. Section 2.2.3.3 describes the relationship between capillary pressure, wettability, and IFT. In general, if a surfactant alters the wettability of a rock matrix, a reduction in IFT lowers the capillary pressure and consequently weakens the process of oil recovery by imbibition. Lowering of the IFT is inevitable while introducing a surfactant in the system. The balance between the individual contributions of a surfactant towards wettability alteration and IFT reduction eventually dictates the potential of that surfactant in improving oil recovery by the process of imbibition. Hence, it is essential to measure the IFTs for each surfactant at the specified concentrations. This section discusses the IFT measurement experiments performed during this research.

5.1 Experimental Method and Setup

The primary objective of the experiments described in this section was to measure the IFT of Shale A oil and frac water without surfactant and investigate the role of adding surfactant to the frac water in lowering the overall IFT between the fluids. The Dataphysics OCA 15 Pro, used for the contact angle measurements, was also used for

the IFT measurements. The pendant drop method was used to calculate the IFTs. The details of the pendant drop method shall be discussed in this sub-section.

5.1.1 Experimental Setup

An experimental setup similar to that of the contact angle experiments was used for the IFT measurements. One notable difference between the setups of these experiments was the exclusion of the shale surface for the IFT measurements as it is not required for IFT measurements. **Fig. 27** shows the schematic of the experimental setup used for the IFT measurements. The J-shaped needle connected to the syringe containing Shale A oil dispenses a droplet of oil in a cuvette containing the fracture fluid. A light source illuminates this droplet and the high resolution camera captures this process and transfers the data to the computer which analyses the data to calculate the IFT. **Fig. 28** shows an actual experiment in progress. A straight needle can be used to measure the surface tension of a fluid in air as a regular pendant drop is formed in this case. On the other hand, an inverted pendant drop as shown in Fig. 27 is formed when the IFT of a lower density fluid (oil) in the presence of a higher density fluid (water) is measured. Therefore, the use of a J-shaped needle becomes necessary in such IFT studies.

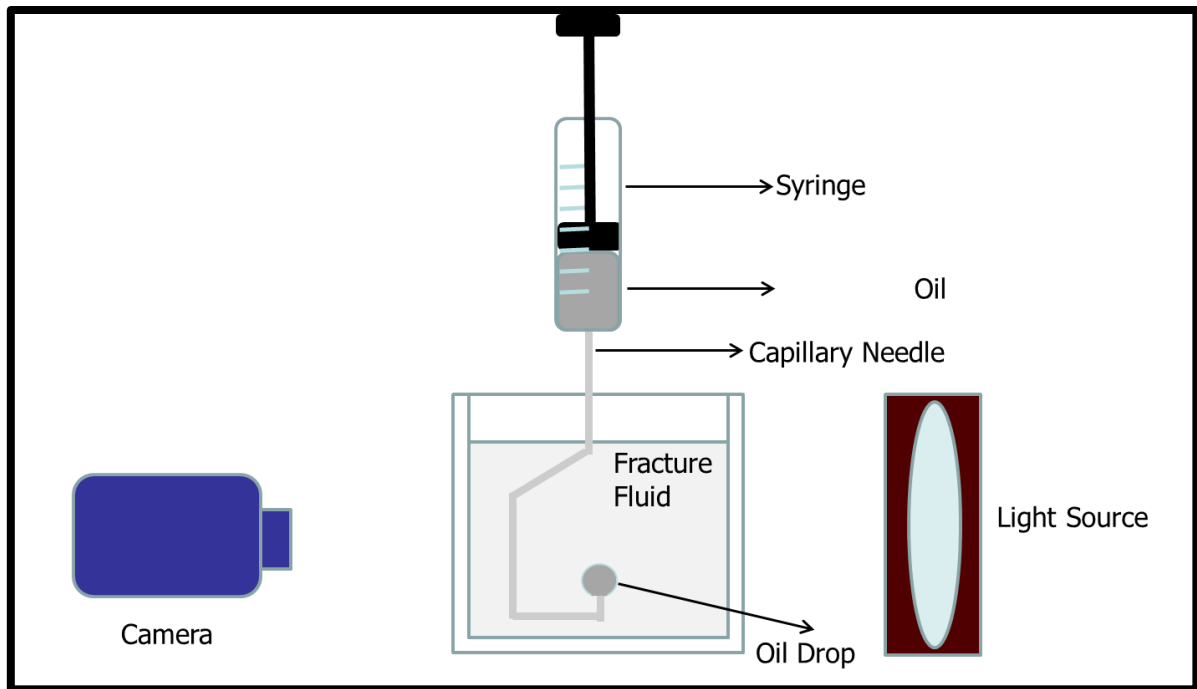


Fig. 27—Schematic of the experimental setup used for IFT measurements

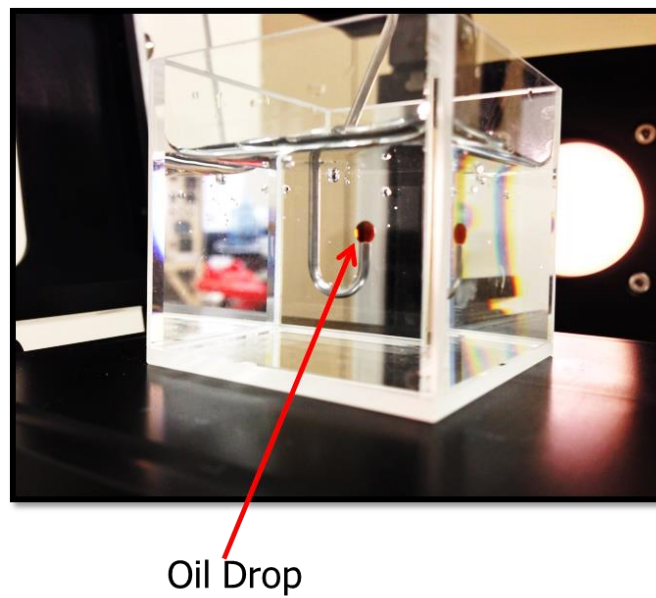


Fig. 28—Actual picture of an experiment performed to measure IFT

5.1.2 Pendant Drop Method and Device Calibration

The pendant drop method is a popular technique used in the industry to measure IFTs of fluids as long as ultralow IFTs are not achieved. For ultralow IFTs, an alternative technique such as the spinning drop method is necessary. For the purpose of IFT measurement of the surfactant concentrations studied in this research, the pendant drop is the most practical and easily implemented approach. The pendant drop method calculates the IFT by analyzing the shape of the fluid droplet. Fig. 27 shows the suspended droplet of fluid which experiences opposite acting forces of gravity and interfacial tension. The force due to IFT is proportional to the circumference of the needle which can be equated to the gravitational force as shown in Eq. 14.

$$F_g = \pi d \sigma \sin \theta \dots \dots \dots (14)$$

where F_g is the force exerted due to gravity, d is the diameter of the needle, σ is the IFT, and θ is the angle of contact of the fluid with the tube.

At the maximum weight of the droplet, the limit of Eq. 14 in which the angle of contact goes to 90° provides the IFT of the fluids (Eq. 15).

$$F_g = \pi d \sigma \dots \dots \dots (15)$$

Prior to the start of any experiments, device calibration was performed in order to ensure accurate IFT measurements during the study. The surface tension of distilled water in air was measured to calibrate the device. Vargaftik et al. (1983) reported values of surface tension of water at different temperatures in the “International Tables of Surface Tension of Water”. The surface tension of distilled water measured in the lab was compared to the standard values reported by Vargaftik et al. (1983).

Fig. 29 shows the image of a water droplet which is used to calculate the surface tension of water by the device. At a temperature of 72 ° F (or 22.2 ° C), the surface tension was reported as 72.15 mN/m. This value was compared with the surface tension values presented in the standard table provided by Vargaftik et al. (1983) as shown in **Table 6**. The measured value of 72.15 mN/m fell in the range of values reported in the standard table meaning that the device was calibrated and was calculating accurate values of surface tension.

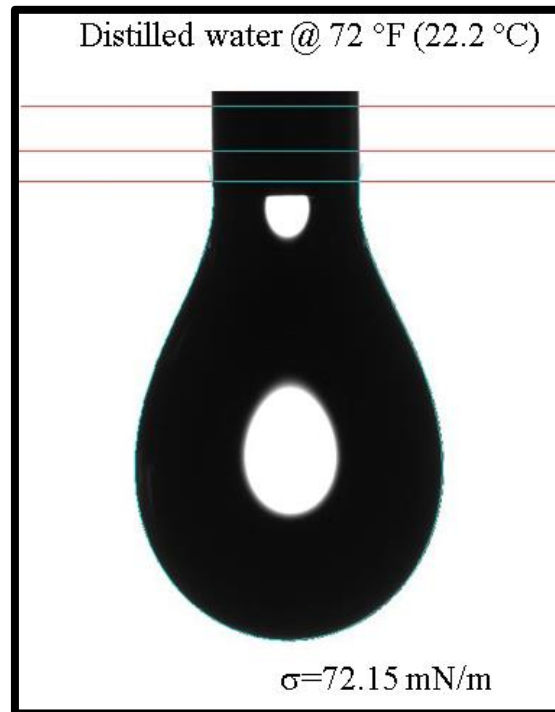


Fig. 29—Image of a droplet of water used to calculate the surface tension of water in air during the process of device calibration

Table 6—Standard surface tension values for water at different temperatures

Surface tension of water as a function of temperature	
t °C	$\sigma \cdot 10^{-3} \text{N/m}$
0.01	75.64
5	74.95
10	74.23
15	73.50
20	72.75
25	71.99
30	71.20
35	70.41

After successfully calibrating the device by measuring the surface tension of distilled water, the next step was to set up the device for IFT measurements as explained in section 5.1.1 and perform the IFT experiments for each surfactant at concentrations of 0.2 gpt, 1.0 gpt, and 2.0 gpt.

5.2 Results and Discussion

Similar to that in the contact angle experiments, the first objective of the IFT measurements was to measure the IFT of Shale A oil and frac water without any surfactant added to it. The IFT of Shale A oil and frac water alone was reported as 21.78 mN/m at the reservoir temperature of 165 ° F. Addition of surfactant to frac water lowered the IFT of the system regardless of the concentration used. The measured IFT values for the surfactants are summarized in **Table 7**. Increasing the concentration of

surfactant resulted in a greater decrease of IFT regardless of the surfactant type. In order to investigate the impact of concentration on IFT, 20 gpt of Surf B was added to the frac fluid and the IFT was measured. A comparison of IFT measurements for Surf B at concentrations of 2 and 20 gpt are shown in **Fig. 30**. It is clear that addition of surfactant to the frac fluid reduces the IFT of the system, and this trend continues until the critical micelle concentration (CMC) is reached. After CMC is reached, further addition of surfactant would not lower the IFT of the system any further.

Table 7—Summary of IFT results for all surfactants (IFT in mN/m)

Concentration	Frac Water	Surf A	Surf B	Comp B	Comp C	Comp A
0.2 gpt	21.78	16.7	16.17	11.41	7.73	5.95
1 gpt		13.22	10.27	8.13	5.04	4.24
2 gpt		9.82	8.69	6.97	4.79	3.86

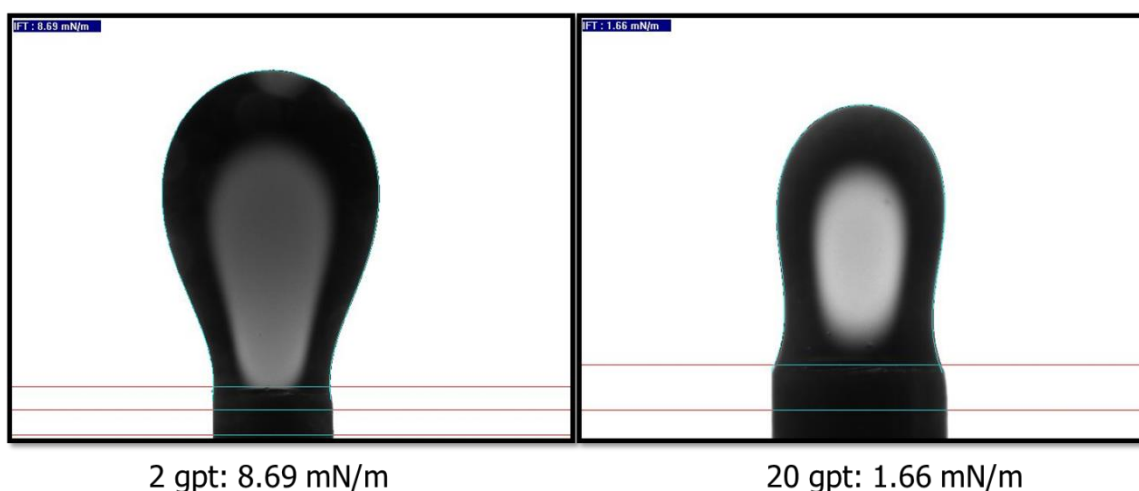


Fig. 30—Comparison of IFT values for Surf B at two different surfactant concentrations

Fig. 31 summarizes different values of IFT reduction achieved by the surfactants at different concentrations. Comp A was most effective in reducing the IFT of the system, followed by Comp C, Comp B, Surf B, and Surf A. The effectiveness of these five surfactants in reducing IFT of the system seems to align with their potential of lowering the contact angle, except for Comp B. In section 4.4, it was shown that among the complex nano-surfactants, Comp B was more effective in altering wettability of the Shale A COBR system than Comp C. However, with regards to IFT reduction, Comp C was found to be more effective than Comp B, regardless of the concentration.

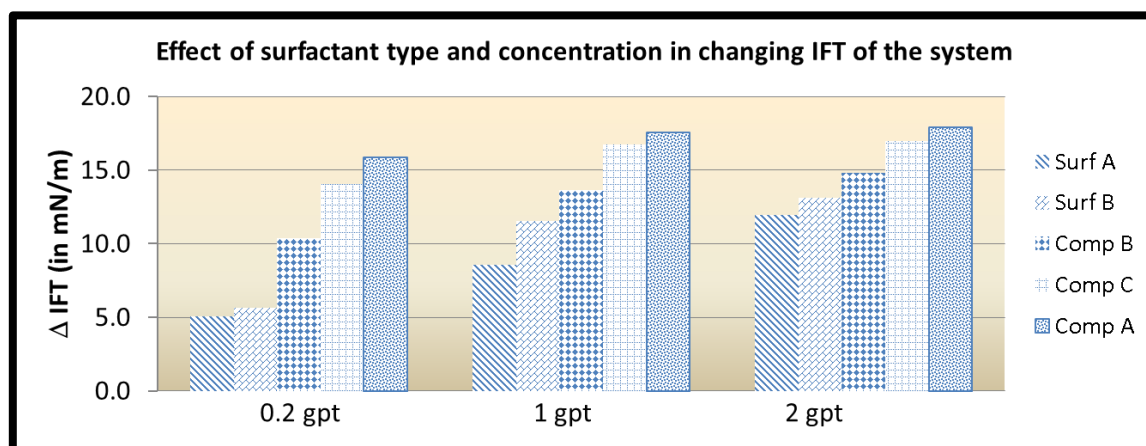


Fig. 31—Summary of IFT reduction due to surfactant type and concentration

Figs. 32-34 show the images of oil droplets in surfactants systems of varying concentrations. These images are analyzed by the device to calculate the IFT of the system using the pendant drop method. The change in the shape of the drop due to reduced IFT is very evident in these images. Overall, the complex nano-surfactants are

more effective in reducing the IFT of the system as compared to the traditional nonionic surfactants.

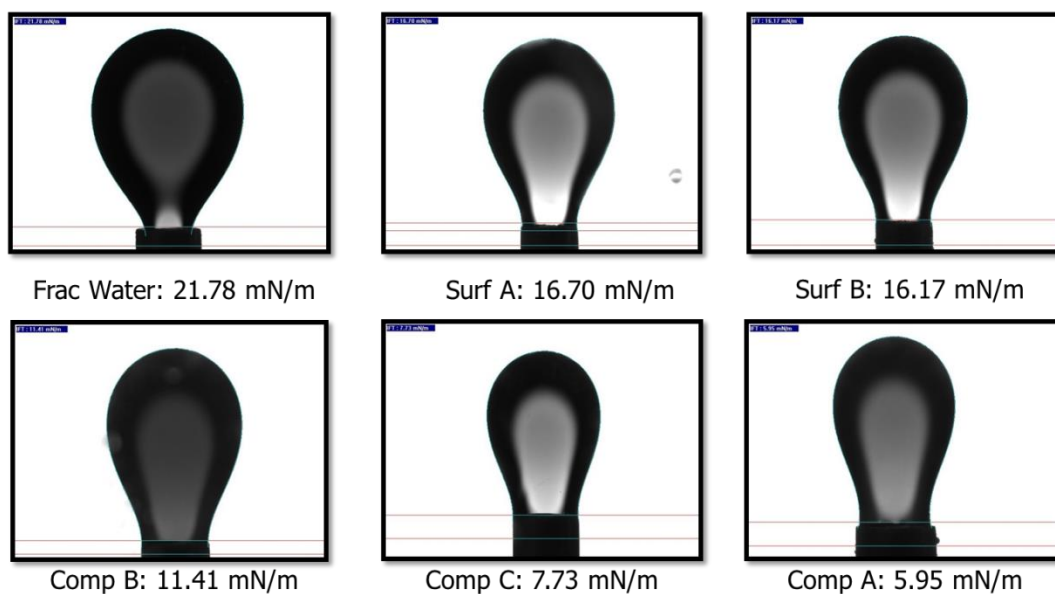


Fig. 32—Change in the shape of oil droplet and reduction in IFT due to addition of surfactant at 0.2 gpt

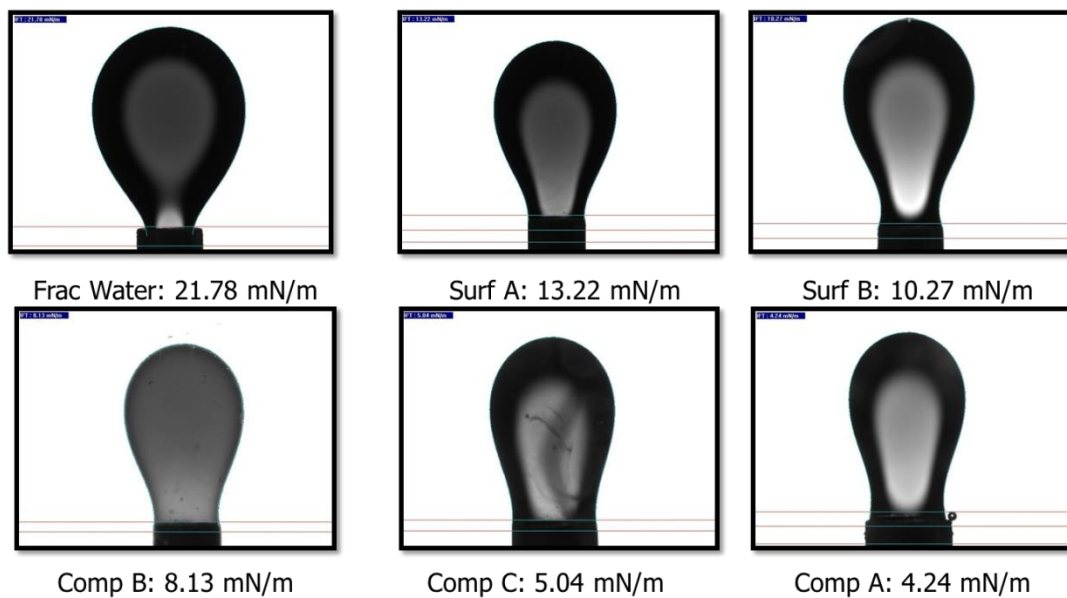


Fig. 33—Change in the shape of oil droplet and reduction in IFT due to addition of surfactant at 1.0 gpt

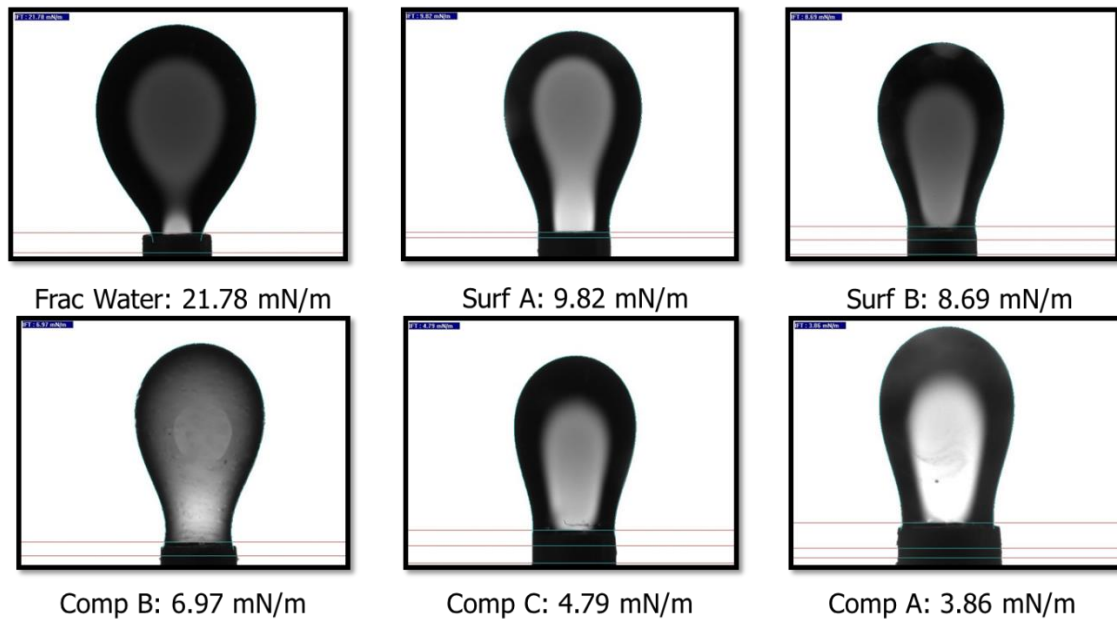


Fig. 34—Change in the shape of oil droplet and reduction in IFT due to addition of surfactant at 2.0 gpt

Although the primary objective of this research work is to study the wettability alteration potential of surfactants, it was important to understand the impact of using surfactant to the IFT of the system. As discussed earlier, the capillary forces of a rock system depend strongly on the wettability and the IFT of the system. The reduction in IFT results in lowering the capillary pressure of the system. Generally speaking, this is usually desirable in a conventional system where fluids get displaced from the pore network due to viscous forces. However, when the dominant mechanism of recovery is solely imbibition, in a water-wet system, lower capillary pressure decreases the rate of water imbibition and can significantly affect oil recovery. This section investigated the “side effect” of adding surfactant which is reduced IFTs. **Fig. 35** shows the ability of surfactants in lowering the IFT of the system relative to each other.

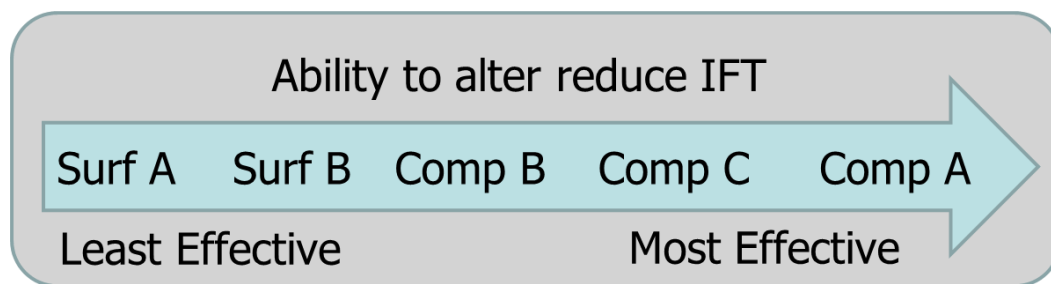


Fig. 35—Comparison of the ability of surfactants to alter wettability in shale

In summary of sections 4 and 5, it can be concluded that Comp A is the most effective surfactant while Surf A is the least effective surfactant as far as the abilities to alter wettability and reduce the IFT are concerned. Having acquired the necessary information about wettability and IFT of the system and the impact that these surfactants

have on these parameters, the next step in this research was to perform spontaneous imbibition experiments using these surfactants and analyzing the experiments with the help of the CT scanner.

6. SPONTANEOUS IMBIBITION EXPERIMENTS WITH SURFACTANTS

The results in sections 4 and 5 so far have demonstrated the potential or the lack of each tested surfactant in altering wettability in shales. However, the only way to find if wettability alteration can improve the performance of shale reservoirs or not is by relating the wettability and IFT results to some sort of a performance metric like change in fluid saturations or oil recovery from a core. One practical approach to obtain this information in the laboratory is to conduct spontaneous imbibition experiments under a CT scanner and analyzing the CT images as well as measuring oil recoveries during the experiments. Application of CT methods during spontaneous imbibition experiments can provide detailed information regarding changes in spatial fluid saturations due to imbibition activity. This section discusses the experimental setup, design, and results from spontaneous imbibition experiments of surfactants in Shale A cores using CT methods.

6.1 Experimental Method and Setup

6.1.1 Core Sample Description and Preparation

The samples used for the spontaneous imbibition tests were carefully aged and prepared for the spontaneous imbibition experiments. The core samples were aged in Shale A oil at reservoir temperature for over 12 months. The long aging process was an important step in order to ensure restoration of native wettability in these originally unpreserved core samples. **Fig. 36** shows the conventional oven used in the aging

process of the core samples. These core samples were also CT scanned prior to the aging process.



Fig. 36—Aging of core samples in a conventional oven

It is a difficult task to gauge the impact of the aging process quantitatively in these ultra-tight shale samples as there is significant uncertainty regarding the initial fluid saturation of a sample prior to the aging process. However, the impact of aging is apparent qualitatively while comparing the appearance of samples before and after aging as shown in **Fig. 37**. The aged sample bears a darker appearance while the non-aged sample shows a lighter color.

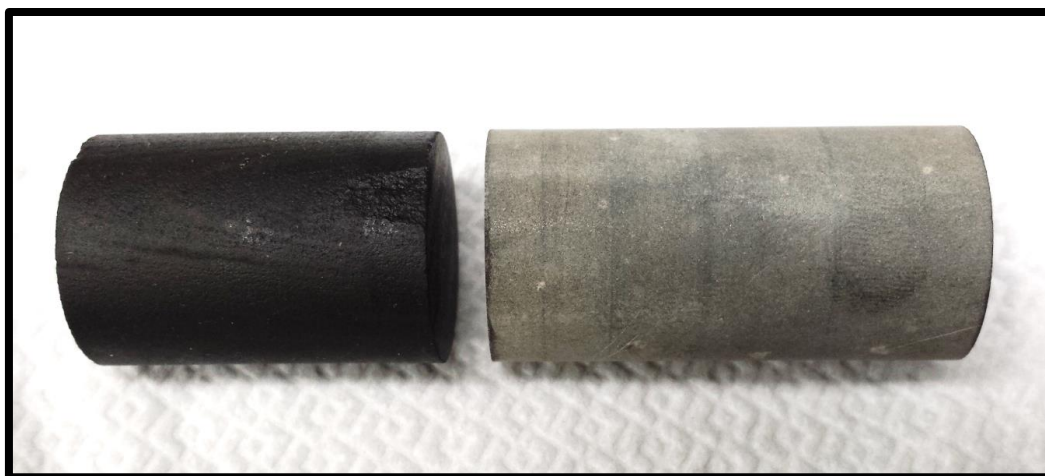


Fig. 37—Comparison of an aged (left) vs. non-aged (right) shale core sample

Since the samples were originally not preserved, the samples most likely do not contain any hydrocarbons in them depicted by a lighter color. However, during the process of aging the unpreserved sample over a period of 12 months, oil most likely imbibes into the sample due to its state of intermediate wettability.

6.1.2 Experimental Method

A spontaneous imbibition experiment involves allowing a sample to sit in a particular fluid and investigate if any fluid imbibes into the sample freely due to capillary forces without any addition pressure support. Section 2.2.3.1 explains the process of spontaneous imbibition in detail. The experimental method was designed to achieve two objectives which were to investigate the change in fluid saturations inside the core during the experiment using the CT scanner and visually verify oil recovery due to spontaneous imbibition of frac water. Although measuring oil recovery during the experiment was not the primary objective, final oil recovery was measured nonetheless.

The change in fluid saturations during the experiment can be calculated if the core is CT scanned before, during, and at the end of the experiment. The change in CT numbers can be correlated to fluid saturations using Eqs. 10 and 11 as long as the porosity of the sample is known. The porosity of the sample is available from core analysis reports. Besides, these samples were CT scanned before the aging process. Therefore, the porosity of the samples can also be obtained by CT analysis using Eq. 9.

Oil expulsion during the course of the experiment can be visually verified if the experiment is conducted in a transparent vessel. Close monitoring and periodic CT scanning of a sample is essential in order to capture subtle changes in the fluid saturation of the sample due to spontaneous imbibition.

6.1.3 Experimental Setup

First of all, the dimensions of the aged sample were measured and the sample was weighed. A high temperature resistant clear glass vessel was used to conduct the experiment. A layer of glass beads was put at the bottom of the container. The layer of glass beads at the bottom was put in order to provide stability to the core sample during the entire experiment. **Fig. 38** shows a core sample inside the container prior to the start of the experiment.

The sample was then put under the CT scanner to capture the CT response prior to the experiment. Shale A oil and brine samples were also separately CT scanned to record the CT responses of the oil and brines individually. Thereafter, a specific brine sample heated up to reservoir temperature was poured into the container and the container was then kept in an oven maintaining reservoir temperature. Routine CT scans

were conducted for a period of nine days. Oil expulsion, if any, was visually monitored during the experiment.

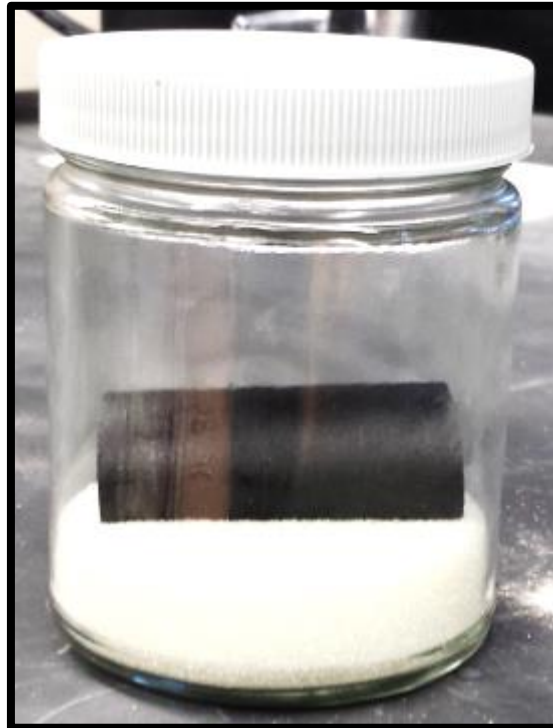


Fig. 38—Sample configuration used in the spontaneous imbibition experiment

At the end of the experiment, the oil expelled due to imbibition of brine was carefully transferred into a graduated cylinder using a syringe and the core sample was weighed again. This setup was followed for each of the five surfactants and frac water. The oil recoveries were compared and CT image analysis was performed to understand the effect of each surfactant in improving recovery performance.

6.1.4 Equipment and Chemicals

6.1.4.1 Equipment

A Mettler Toledo XA105 analytical balance was used to measure weight of the core samples. This analytical balance can measure the weight of object up to 220 grams with a readability of 0.01 mg. A conventional oven was used to maintain the reservoir temperature during the experiment. A Toshiba Aquilion TSX-101A CT scanner was used to CT the sample at routine intervals. Fig. 39 shows the CT scanner and the user console. This brand new state-of-the-art CT scanner was recently acquired by Texas A&M University in 2013.



Fig. 39—Toshiba Aquilion TSX-101A CT scanner

The CT scan protocol parameters used in this experiment are shown in **Table 8**. A helical scan was used with a rotation time of one second. The slice thickness was 0.5 mm with an interval of 0.3 mm between each slice. Since the core samples used were small with a diameter of around an inch, a small-small (SS) field of view (FOV) was used for optimum clarity in the CT image with a diameter of 170.2 mm. The kV and the mA of the scans were kept at 135 and 280 respectively. The CT image analysis was performed using an open source software package known as ImageJ.

Table 8—CT scan protocol parameters used

Scan Type	Helical
Rotation Time (seconds)	1
Detector Coverage (mm)	11
Detector Rows	16
kV	135
mA	280
D- FOV (mm)	170.2
Slice Thickness (mm)	0.5
Interval (mm)	0.3

6.1.4.2 Chemicals

The experiments were performed with frac water alone and brines enhanced with each of the five surfactants separately at 2 gpt concentration. Lower concentrations of surfactant were not tested as the objective of this phase of the research was to investigate and compare the potential of these surfactants at similar conditions.

The surfactant enhanced brines used in these experiments contained an additional chemical along with all the other chemicals which were added to the brines for the

contact angle and IFT experiments. This chemical, called a dopant or doping agent, is a trace impurity element which can be added to another substance to change the electrical or optical properties of that substance. A dopant is added to the brine to enhance the CT image contrast between oil and brine inside the core sample during the experiment.

Potassium iodide (KI) was used in these experiments as a dopant. Since shale samples typically have low porosity, the use of dopant for these experiments is necessary in order to see any change in CT images due to imbibition. The CT responses of water and oil are not drastically different and without a dopant, changes in the CT images would most likely not be observed even if there is significant change in phase in the tiny pore volume due to imbibition as the subtle change in CT response in the pores would be masked by the predominant CT response of the rock matrix.

6.2 Results and Discussion

6.2.1 Preliminary Results

This sub-section discusses the initial findings related to the spontaneous imbibition experiments. **Tables 9 and 10** summarize some essential parameters measured and calculated prior to the start of the spontaneous imbibition experiments. Table 9 shows the CT responses obtained for air, brine, and oil. CT response is recorded in terms of CT numbers or Hounsfield units (HU). The CT numbers for these phases are calculated by the CT scanner using Eq. 8. It is important to note that the CT value for brine is 2500, which is way different than the typical CT number of water, which is considered to be 0. This discrepancy in the CT values is desirable as it allows great CT image contrast between oil and brine, and is achieved due to the addition of dopant to the

brine. The Shale A oil showed a CT value of -185. The CT value of air was measured as -1SPE-, indicating that the CT scanner was properly calibrated.

Table 9—CT numbers of different phases present in the experiments

Phase	CT values
Air	-1SPE-
Brine	2500
Oil	-185

Table 10—Specifications of samples used in the experiments

Sample #	Brine	Average Dry Core CT #	Average Aged Core CT #	Dia.	L	ϕ	ϕ	Pore Vol.	Weight (Before)
				cm	cm	Core	CT		
1	Frac Water	2464.784	2527.408	2.54	5.08	0.083	0.077	2.126	67.74
2	Surf A	1618.495	1683.652	2.54	2.85	0.090	0.080	1.299	33.30
3	Surf B	1781.648	1858.458	2.54	5.59	0.108	0.094	3.052	68.91
4	Comp A	1890.168	1959.455	2.54	4.78	0.095	0.085	2.306	59.61
5	Comp B	1775.349	1844.173	2.54	4.57	0.092	0.084	2.127	53.21
6	Comp C	2058.871	2136.127	2.54	3.86	0.105	0.095	2.046	47.66

Table 10 specifies certain parameters for each sample which are used during the analysis of results obtained in the experiments. These samples were CT scanned prior to the aging process. The CT responses obtained during those scans is referred to in the table as dry core CT number. This value is used along with value in Table 9 to obtain the porosity of the sample using Eq. 9.

It is important to mark the discrepancy between the porosities reported in the core analysis report and the CT analysis. The porosity values obtained from the CT analysis were lower as compared to that obtained from the core analysis report, across all samples. The most likely explanation for this observation is the fact that the aging process does not potentially guarantee that all the pores in the sample get filled with oil. It is possible that even after aging these samples for over 12 months, air remains trapped in the pores. Since Eq. 9 assumes that air initially present in all the pores is replaced by a liquid phase, the calculated porosity value is likely underestimated. Hence, for all CT image analyses, the porosity reported in the core analysis reports is used.

The dimensions of the samples are also reported in Table 10 which were used along with porosities to calculate the volumetric capacities of the samples. The weights of the samples were measured not for the purpose of any absolute material balance calculations, but for observing any changes due to brine imbibition.

6.2.2 CT Scan Results

The CT scan results are presented and discussed separately for each tested sample. In total, CT results for frac water and five surfactant enhanced brines at a concentration of 2 gpt are discussed in this sub-section. The initial water saturation s values of these samples are unknown since initial water saturation is rather difficult to measure in these ultra-tight shale cores. However, for the sake of simplicity and ease of comparison of surfactant performance, the initial water saturation of these samples was considered to be negligible as they were put directly in oil only during the aging process.

6.2.2.1 Frac Water

The average CT number of the sample before the start of the experiment is 2527.408 as shown in Table 10. **Table 11** summarizes the average CT response and increase in water saturation (S_w) over a period of 9 days. It was observed that the total increase in water saturation was only 3.28%. Frac water without any surfactant was not able to penetrate into the sample very effectively. However, the intermediate wet shale sample did allow some water to imbibe at a very slow rate which resulted in the slight increase in water saturation. This observation establishes the fact that the state of wettability strongly impacts imbibition performance. Due to a contact angle of around 110° as measured in section 4, the majority of the surface of the pores is wet by oil molecules. This does not allow water to effectively imbibe into the pore system due to a very weak or negative water-oil capillary pressure.

Table 11—CT scan results for frac water

Time (days)	Average Core CT #	S_w
0	2527.408	0.00%
0.0833	2527.8597	0.20%
0.5	2529.93985	1.14%
1	2531.486874	1.84%
3	2532.500779	2.30%
5	2533.691097	2.83%
7	2534.162181	3.05%
9	2534.675917	3.28%

The CT results for this experiment are shown graphically in **Fig. 40**. It can be observed in the figure that CT number increases more rapidly initially as compared to that during late time. One possible explanation for this could be the fact that initially there is a weak but positive water-oil capillary pressure which results in a more rapid imbibition. At late time, the increase in water saturation results in imbibition capillary pressure reducing as well as shown in Fig. 3 and hence, the rate of imbibition slows down. **Fig. 41** shows the CT images of a representative axial slice of sample 1. Visually, it is rather difficult to trace the subtle increase in water saturation in these images except in the bright colored band. However, it is interesting to observe two distinct regions of CT response. This most likely indicates mixed mineralogy in this core sample. The region shown to have a bright colored band in the CT image consists of minerals that provide a higher CT response which might also be more water-wet as compared to the rest of the core sample.

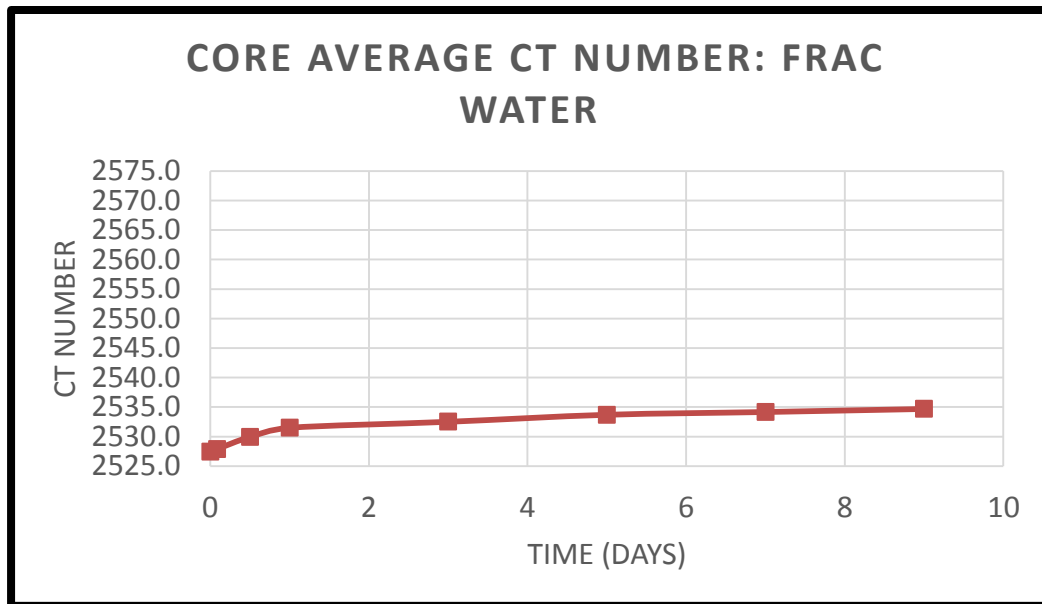


Fig. 40—CT response of shale sample in frac water during the experiment

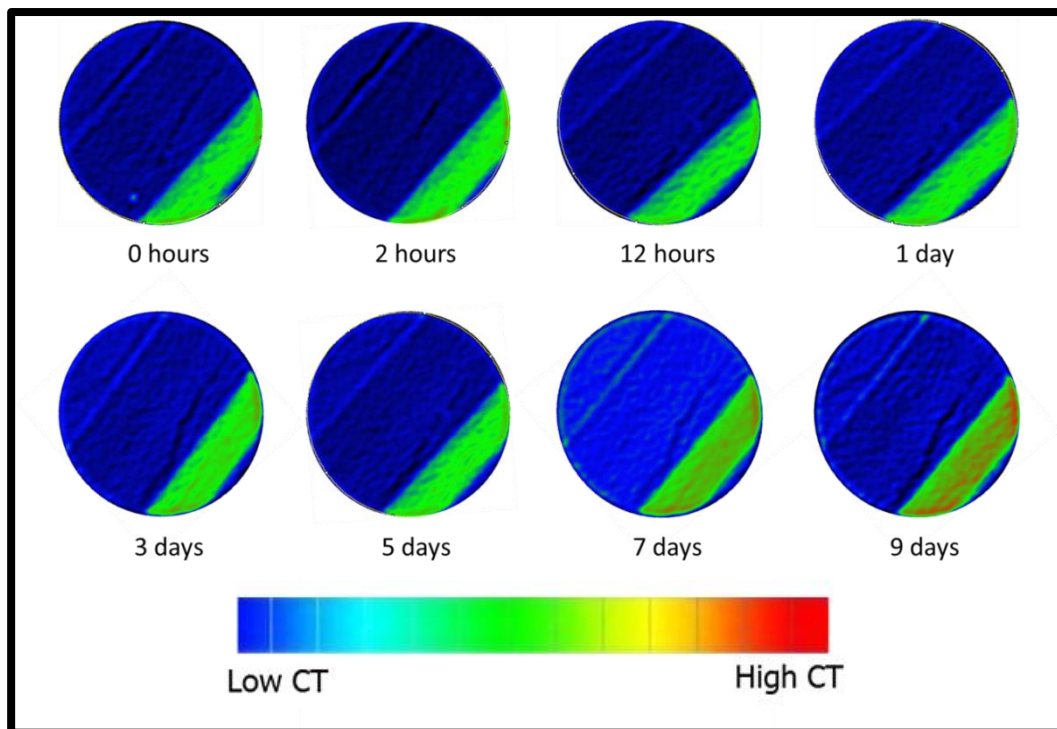


Fig. 41—CT images of an axial representative slice of sample 1

6.2.2.2 Surf A

The average CT number of the sample used with Surf A before the start of the experiment is 1683.652 as shown in Table 10. **Table 12** summarizes the average CT response and increase in water saturation (S_w) over a period of 9 days. It was observed that the total increase in water saturation was about 6.50%. Surf A performed almost twice as good as frac water. The addition of surfactant to the brine allowed for wettability alteration which improved the performance of spontaneous imbibition.

The CT results for this experiment are shown graphically in **Fig. 42**. The trend in CT response is similar to the first experiment in the fact that the rate of imbibition slows as the water saturation increases in the core.

Table 12—CT scan results for Surf A

Time (days)	Average Core CT #	S_w
0	1683.652	0.00%
0.0833	1686.591	1.22%
0.5	1688.644	2.07%
1	1690.764	2.95%
3	1692.517	3.67%
5	1695.479	4.90%
7	1697.017	5.54%
9	1699.3418	6.50%

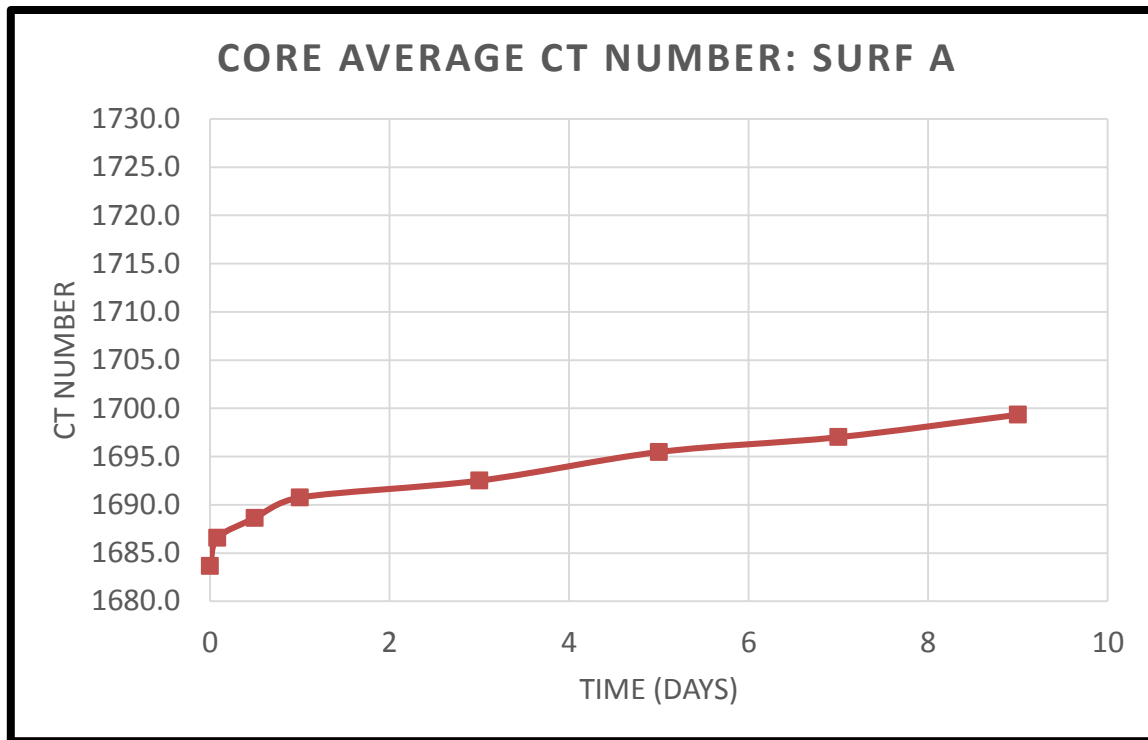


Fig. 42—CT response of shale sample in Surf A during the experiment

Fig. 43 shows the CT images of a representative axial slice of sample 2. The movement of brine due to imbibition is visible in this experiment. Surf A alters the wettability of the matrix system to a certain extent which allows brine to penetrate the matrix. The rate of imbibition is hugely dependent on the extent of wettability alteration and there is a possibility in this case that further imbibition might occur if the core sample is left in the surfactant enhanced brine for longer. It can also be noticed from the CT images that the change in CT numbers occur at the upper part of the core sample. This might be due to the configuration of the experimental setup as shown in Fig. 38 where the surfactant enhanced brine contacts more area in the upper region as compared to the lower region due to the presence of the glass beads.

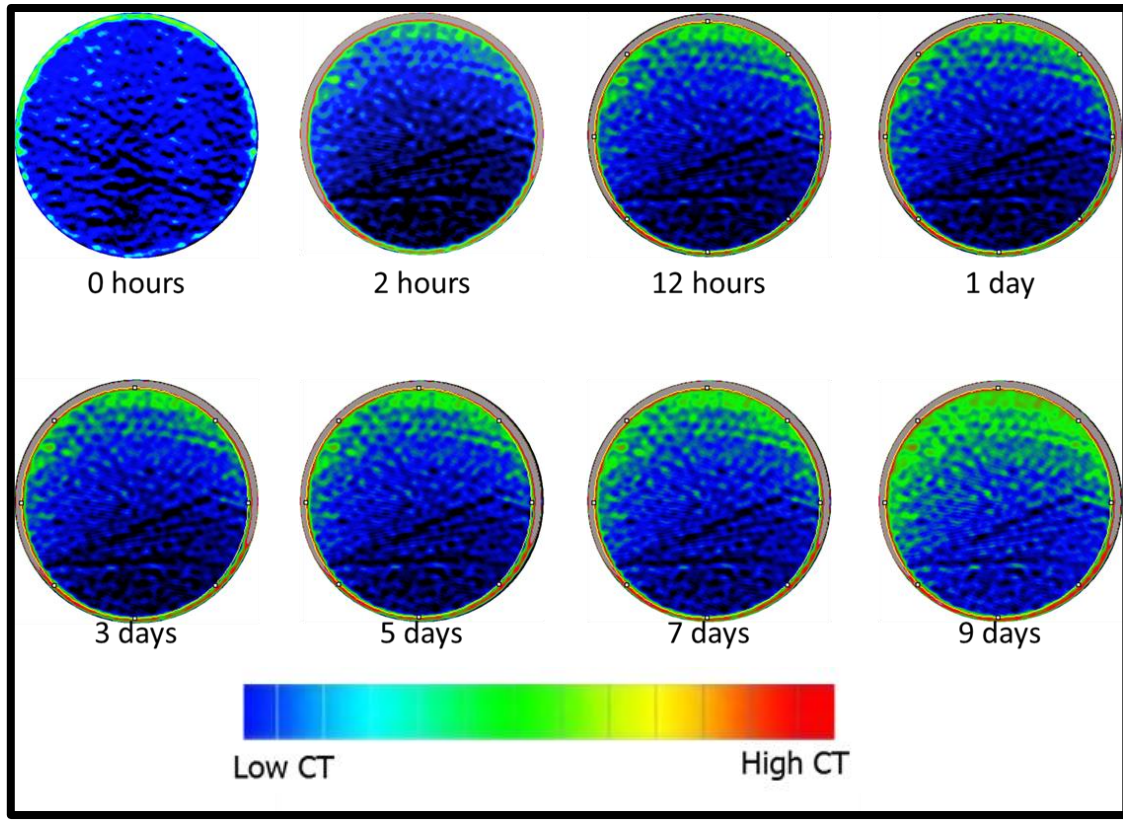


Fig. 43—CT images of an axial representative slice of sample 2

6.2.2.3 *Surf B*

The average CT number of the sample used with Surf B before the start of the experiment is 1858.458 as shown in Table 10. **Table 13** summarizes the average CT response and increase in water saturation (S_w) over a period of 9 days. It was observed that the total increase in water saturation was about 12.45%. Surf B performed significantly better than Surf A in imbibition performance just like in the wettability experiments. In the contact angle experiments, it was found that Surf B has the potential to alter the wettability of the rock to a relatively strongly water-wet state. This allows for it to perform better as compared to Surf A in the imbibition of the brine in the sample.

The CT results for this experiment are shown graphically in **Fig. 44**. The CT response shows a continuous upward trend and most likely, the average CT number would have increased if the experiment was continued for a longer duration.

Table 13—CT scan results for Surf B

Time (days)	Average Core CT #	Sw
0	1858.458	0.00%
0.0833	1860.9937	0.88%
0.5	1866.734	2.86%
1	1873.5231	5.20%
3	1882.0434	8.15%
5	1886.035	9.53%
7	1892.1107	11.63%
9	1894.4952	12.45%

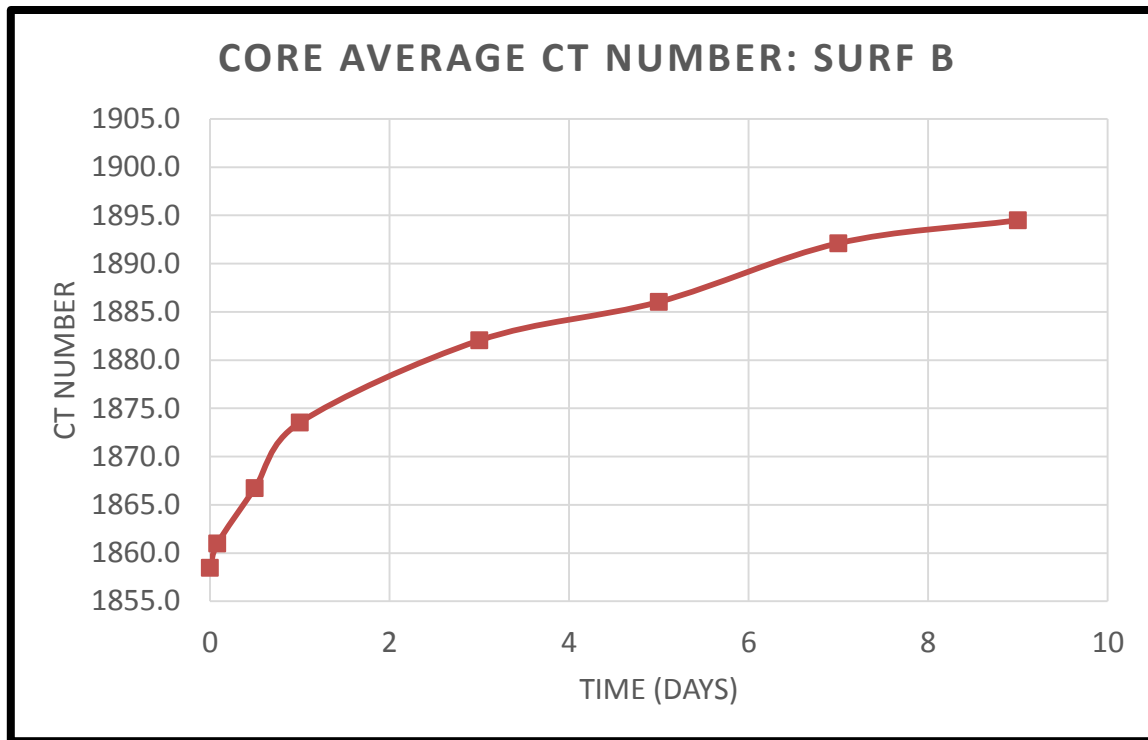


Fig. 44—CT response of shale sample in Surf B during the experiment

Fig. 45 shows the CT images of a representative axial slice of sample 3. The movement of brine towards the center of the sample due to imbibition is visible in this experiment. Surf B alters the wettability of the matrix system considerably allowing brine to penetrate the matrix. A fracture is also seen as a part of the system. There is a possibility that the surfactant contacts more surface area of the shale sample due to the presence of the fracture although the fracture was not visible on the surface of the core sample. Besides, it does not seem like brine moves along the fracture as the CT response of the fracture remains largely unchanged through the experiment. The possibility of this fracture being mineralized is negligible as well since the CT response of the fracture is low indicating the presence of a fluid instead of solid material.

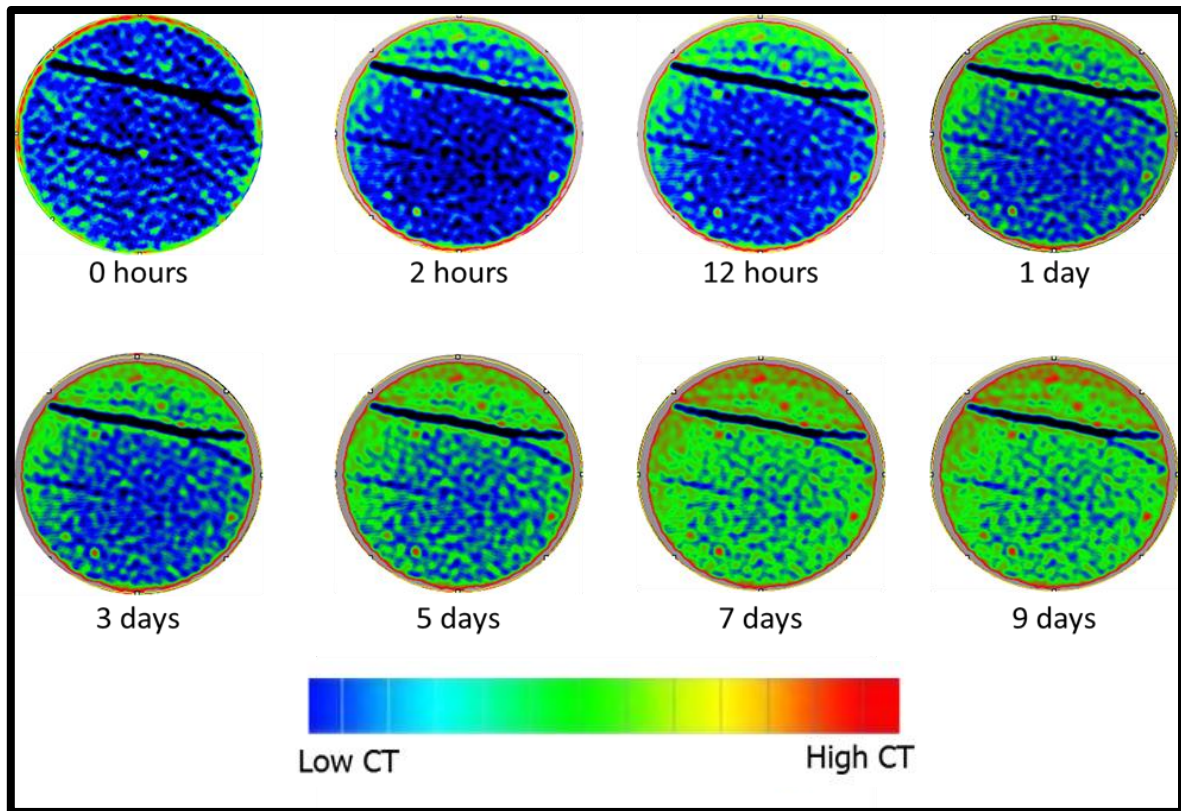


Fig. 45—CT images of an axial representative slice of sample 3

6.2.2.4 Comp A

The average CT number of the sample used with Comp A before the start of the experiment is 1959.455 as shown in Table 10. **Table 14** summarizes the average CT response and increase in water saturation (S_w) over a period of 9 days. It was observed that the total increase in water saturation was about 10.62%. Unexpectedly, Comp A performed slightly poorer than Surf B in imbibition performance unlike in the wettability experiments. In the contact angle experiments, it was found that Comp A has the highest potential to alter the wettability of the rock to a strongly water-wet state. This is contradictory to the performance in this imbibition experiment. Comp A was expected to

perform better than both of the traditional nonionic surfactants. Although Comp A performs better than Surf A, it shows lower imbibition penetration as compared to Surf B.

Table 14—CT scan results for Comp A

Time (days)	Average Core CT #	Sw
0	1959.455	0.00%
0.0833	1961.1222	0.65%
0.5	1965.6373	2.42%
1	1968.6906	3.61%
3	1976.7805	6.77%
5	1979.4849	7.83%
7	1984.0174	9.60%
9	1986.6404	10.62%

The CT results for this experiment are shown graphically in **Fig. 46**. The CT response shows a similar upward trend like in both of the nonionic surfactants indicating that further imbibition of brine is likely if the experiment was continued for a longer duration.

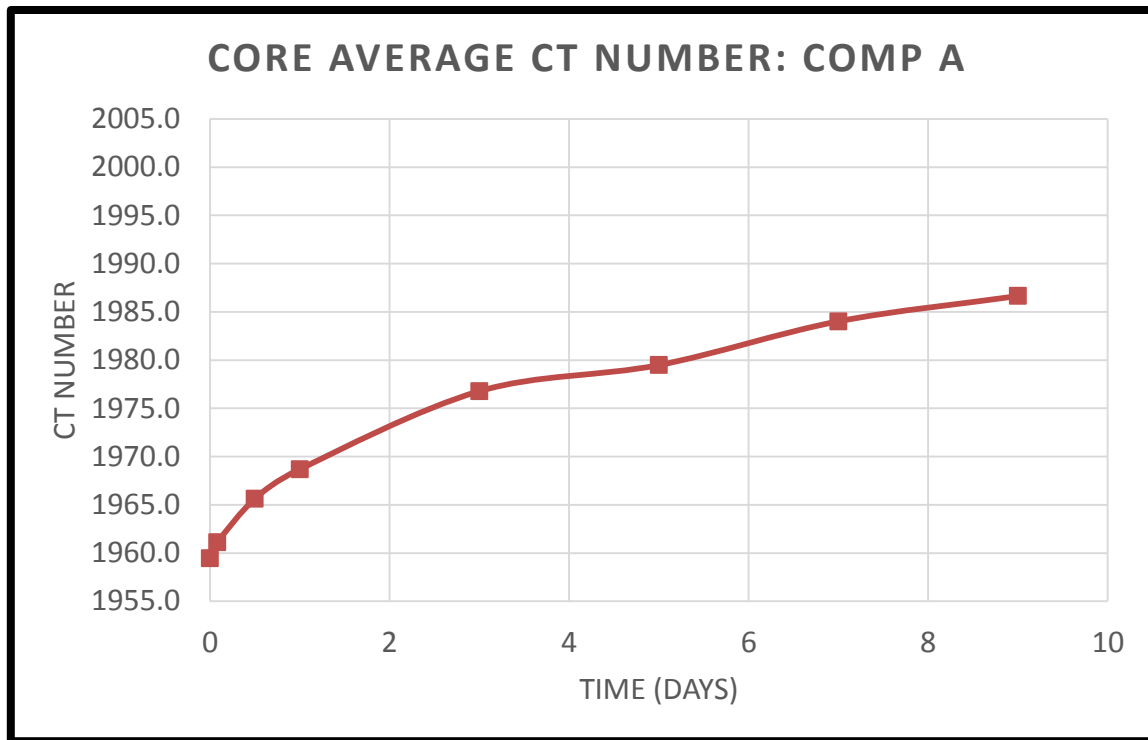


Fig. 46—CT response of shale sample in Comp A during the experiment

Fig. 47 shows the CT images of a representative axial slice of sample 4. The movement of brine towards the center of the sample due to imbibition is also visible in this experiment. Like Surf B, Comp A also alters the wettability of the matrix system, allowing brine to penetrate the matrix. The lower than expected imbibition performance could be due to reduced IFT with Comp A as observed in section 5. The positive effect of wettability alteration on capillary pressure is most likely neutralized to an extent by the reduction in IFT. Lowered IFT resulted in the weakening of the capillary forces and hence, the increase in water saturation in Comp A is lower than that of Surf B.

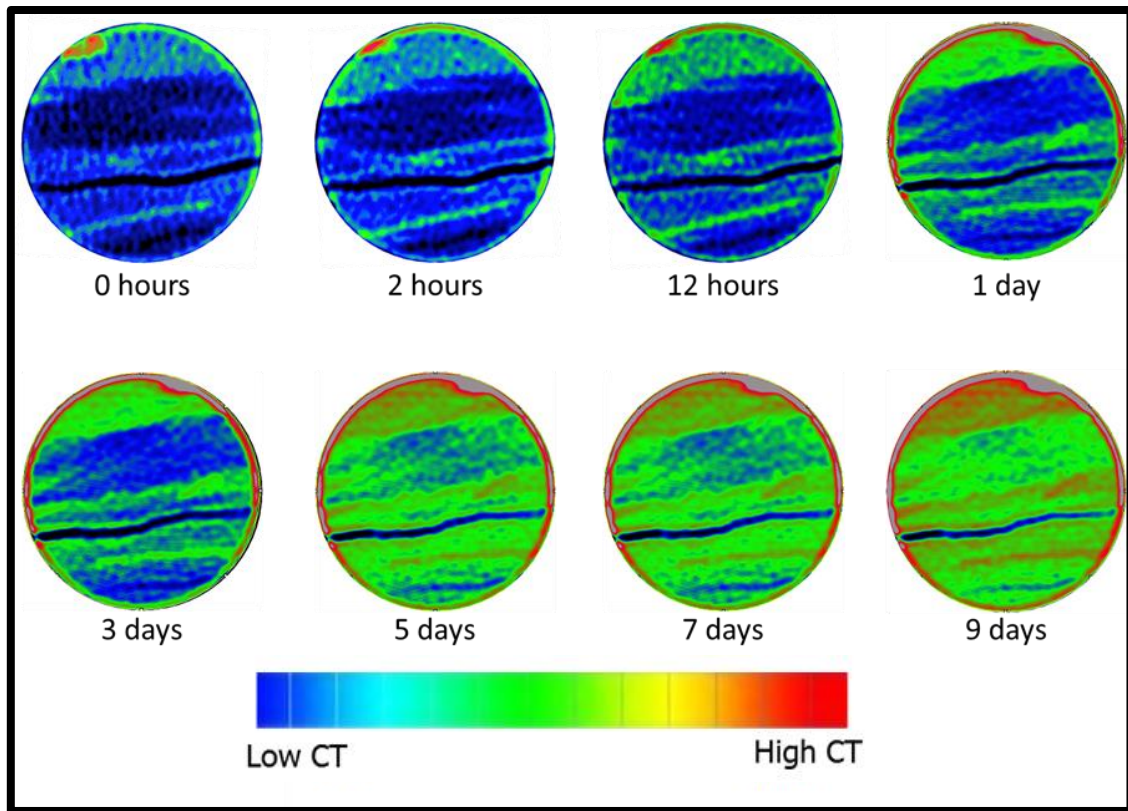


Fig. 47—CT images of an axial representative slice of sample 4

6.2.2.5 Comp B

The average CT number of the sample used with Comp B before the start of the experiment is 1844.173 as shown in Table 10. **Table 15** summarizes the average CT response and increase in water saturation (S_w) over a period of 9 days. It was observed that the total increase in water saturation was about 13.01%. In the contact angle experiments, it was found that Comp B was almost just as competent as Comp A in altering the wettability of the rock to a strongly water-wet state. Besides, Comp B did not lower the IFT of the system as much as Comp A and hence, shows better performance in imbibition recovery as compared to Comp A.

The CT results for this experiment are shown graphically in **Fig. 48**. As compared to Comp A, Comp B is shown to facilitate a faster rate of imbibition at the initial phase of the experiment. After a couple of days, the trends of Comp A and Comp look pretty similar to one another.

Fig. 49 shows the CT images of a representative axial slice of sample 5. The rapid increase in average CT number can be observed in the images. Comp B effectively alters the wettability of the matrix system allowing brine to penetrate the matrix and does not also reduce the IFT as much as Comp A resulting in a stronger positive water-oil capillary pressure. The contribution of the positive effect of wettability alteration is higher than the negative effect of reduction of IFT on the capillary forces. Hence, this complex nano-surfactant allows effective brine imbibition into the shale matrix.

Table 15—CT scan results for Comp B

Time (days)	Average Core CT #	Sw
0	1844.173	0.00%
0.0833	1849.167	2.03%
0.5	1855.371	4.54%
1	1860.476	6.61%
3	1867.834	9.60%
5	1869.679	10.35%
7	1873.987	12.10%
9	1876.2404	13.01%

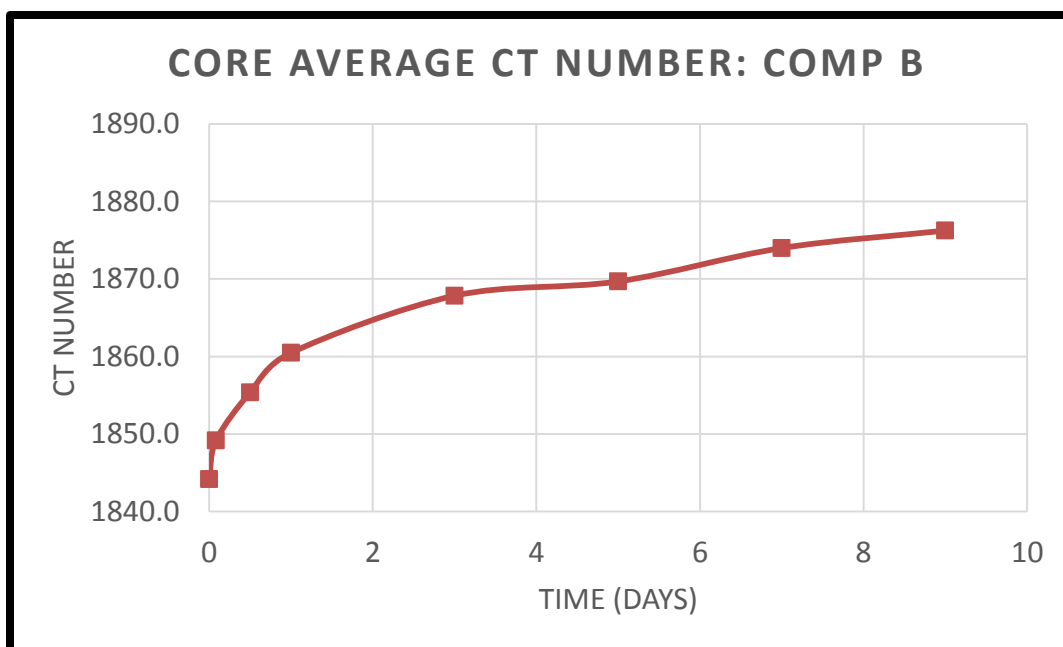


Fig. 48—CT response of shale sample in Comp B during the experiment

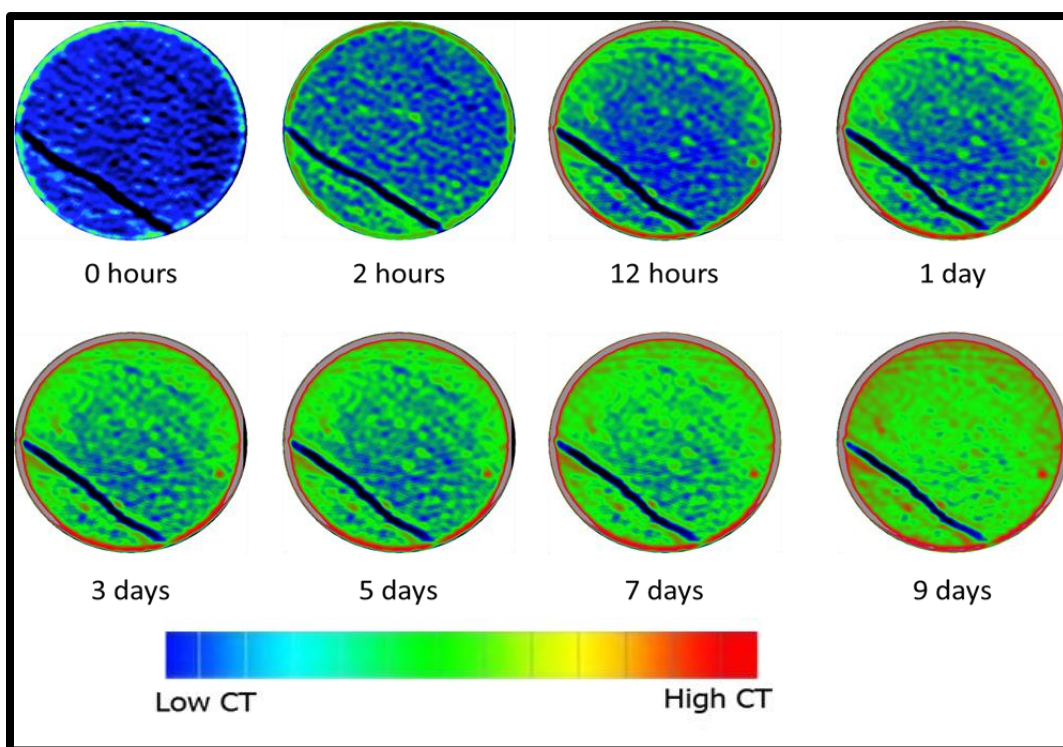


Fig. 49—CT images of an axial representative slice of sample 5

6.2.2.6 Comp C

The average CT number of the sample used with Comp C before the start of the experiment is 2136.127 as shown in Table 10. **Table 16** summarizes the average CT response and increase in water saturation (S_w) over a period of 9 days. It was observed that the total increase in water saturation was about 9.99% making Comp C the worst performing complex nano-surfactant. In the contact angle experiments, Comp C was not able to lower the contact angle as well as Comp A and Comp B at 2 gpt concentration. Besides, the use of Comp C showed lower IFT in the system as much as Comp B and hence, the imbibition penetration performance of Comp C was worse than Comp A and B.

The CT results for this experiment are shown graphically in **Fig. 50**. The rate of increase in CT response is faster at the beginning as compared to the end of the experiment. The CT response continues to gradually increase thereafter, until the end of the experiment.

Table 16—CT scan results for Comp C

Time (days)	Average Core CT #	S_w
0	2136.127	0.00%
0.0833	2138.784	0.95%
0.5	2143.497	2.62%
1	2147.914	4.20%
3	2152.375	5.79%
5	2156.831	7.37%
7	2162.437	9.37%
9	2164.1758	9.99%

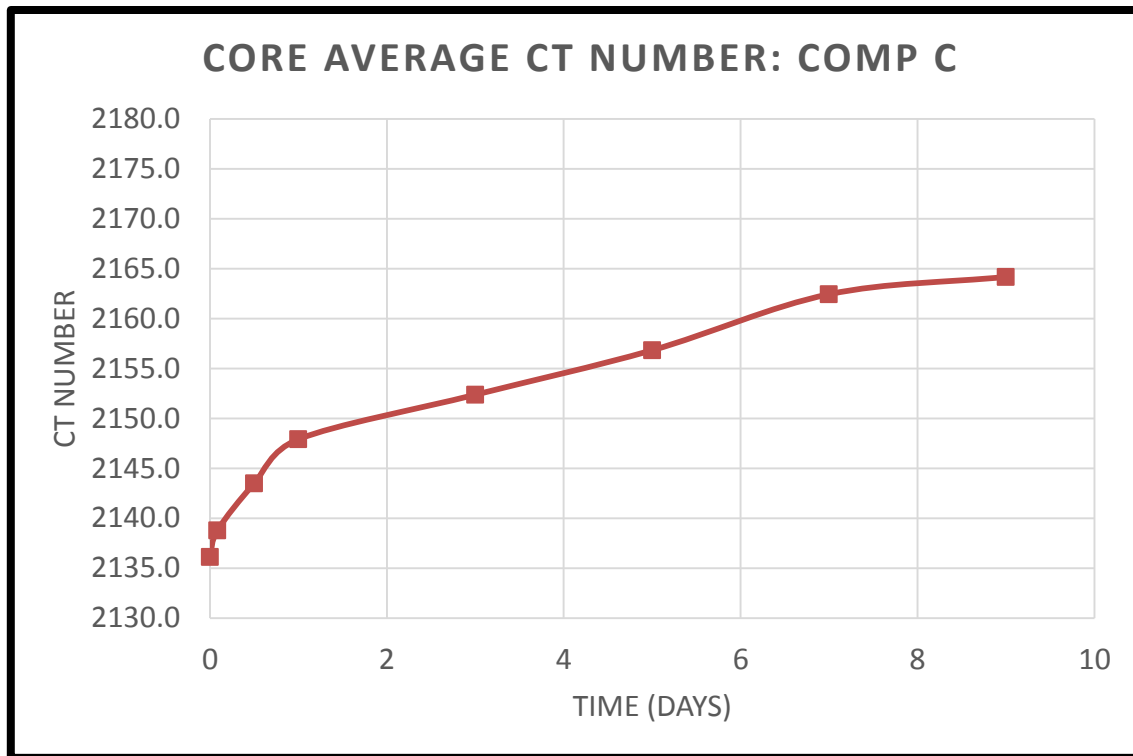


Fig. 50—CT response of shale sample in Comp C during the experiment

Fig. 51 shows the CT images of a representative axial slice of sample 6. A bright spot at the bottom of the core is very noticeable which indicates a very high CT response. This spot is most likely due to some kind of a mineral deposit in the core sample with a very high linear attenuation.

In summary, all surfactants improve the performance of the process of spontaneous imbibition in shale as compared to frac water alone. The impact of the surfactants in improving the performance of imbibition is shown in **Fig. 52**. Surf B unexpectedly showed more potential in improving imbibition performance than Comp A

and Comp C. Overall, Comp B was most effective in improving the imbibition performance in these ultra-tight oil rich shales.

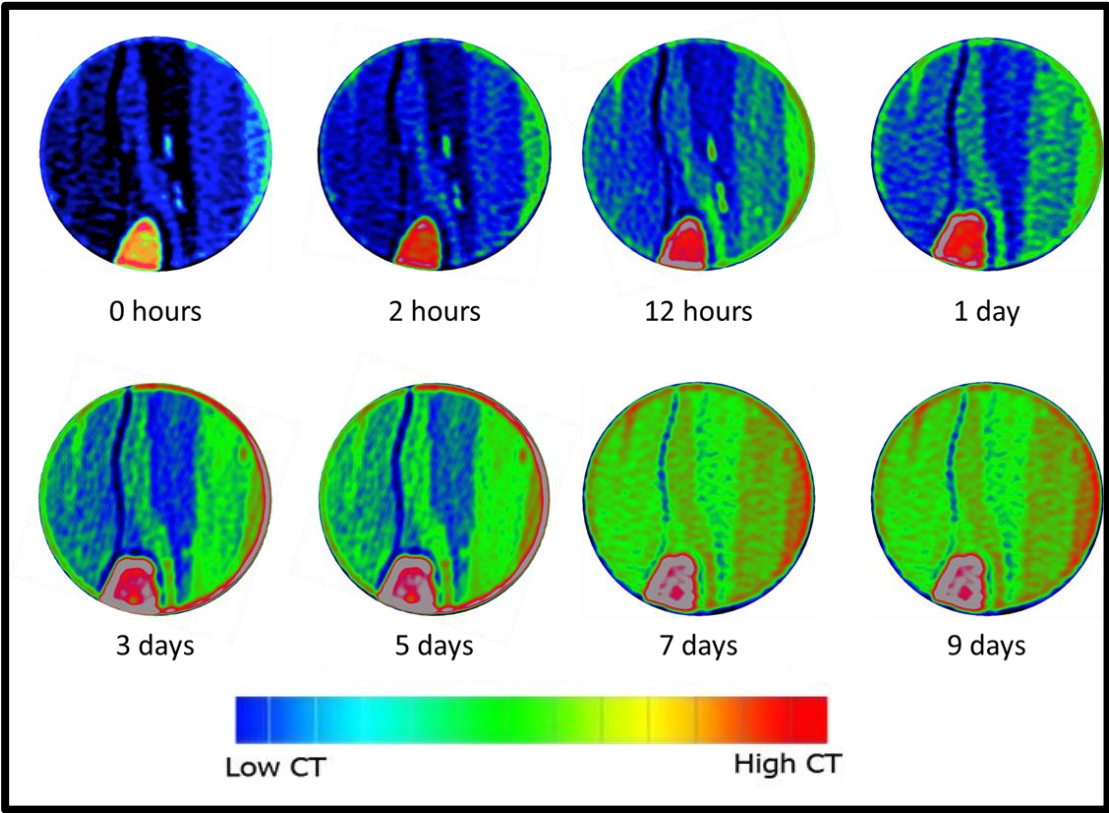


Fig. 51—CT images of an axial representative slice of sample 6

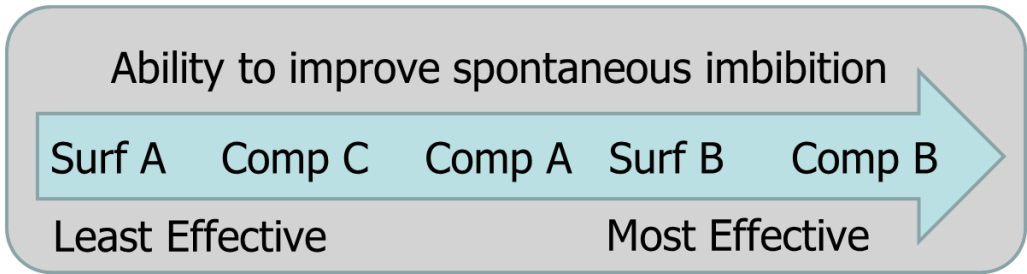


Fig. 52—Comparison of the ability of surfactants to alter wettability in shale

6.2.3 Oil Recovery Results

Along with the results from the CT experiments, it is important to pay attention to the oil recovery result for each of the experiment. Unfortunately, it was not possible to measure oil recovery during the experiments as the periodic oil recovery represented a very small volume which was difficult to measure. However, final oil recovery was measured for the each experiment involving surfactants and the same is presented in this sub-section.

There was negligible oil recovery with frac water and hence, no final oil recovery was measured for sample 1. Since the native wettability of the shale sample is intermediate-wet, some frac water should technically imbibe into the core sample spontaneously expelling oil. This phenomenon was observed in the CT scan results. The same is also seen in **Fig. 53** which is a picture of the core sample near the end of the experiment. Tiny oil bubbles can be seen in the figure on the surface of the core sample. This indicates that some amount of frac water spontaneously imbibed into the core and expelled the oil.



Fig. 53—Oil expelled from the shale core sample due to spontaneous imbibition of frac water

6.2.3.1 *Surf A*

Fig. 54 shows the expulsion of oil from sample 2 due to spontaneous imbibition of brine enhanced with Surf A.

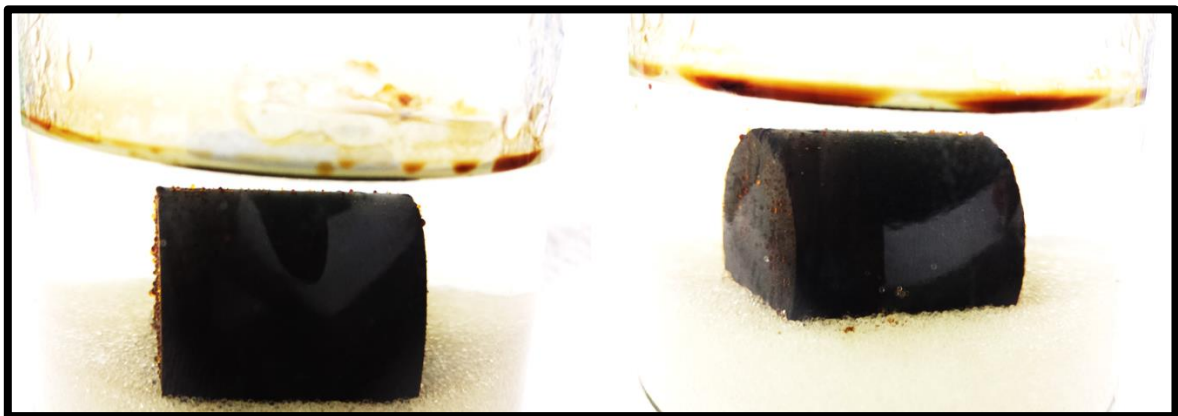


Fig. 54—Oil expelled from the shale core sample due to spontaneous imbibition of Surf A

6.2.3.2 *Surf B*

Fig. 55 shows the expulsion of oil from sample 3 due to spontaneous imbibition of brine enhanced with Surf B.



Fig. 55—Oil expelled from the shale core sample due to spontaneous imbibition of Surf B

6.2.3.3 *Comp A*

Fig. 56 shows the expulsion of oil from sample 4 due to spontaneous imbibition of brine enhanced with Comp A.

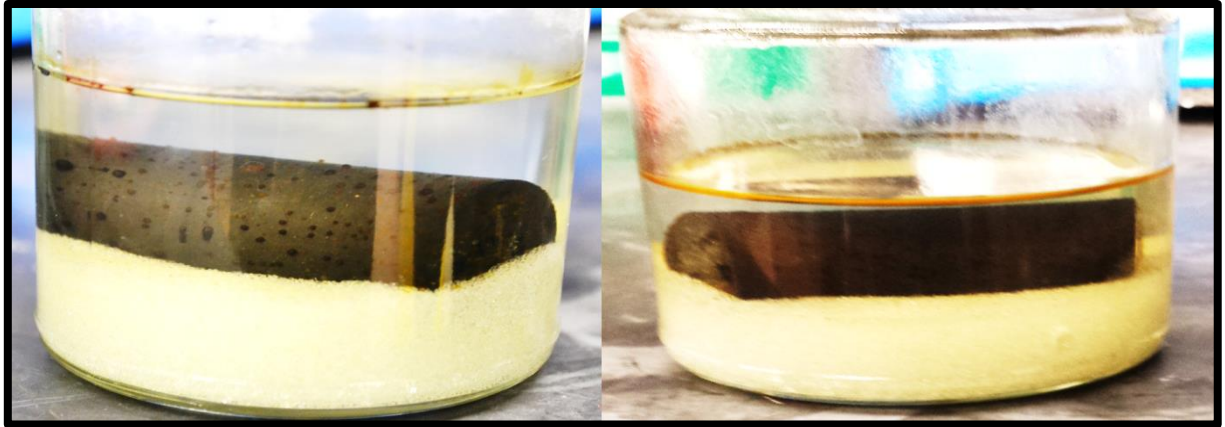


Fig. 56—Oil expelled from the shale core sample due to spontaneous imbibition of Comp A

6.2.3.4 Comp B

Fig. 57 shows the expulsion of oil from sample 5 due to spontaneous imbibition of brine enhanced with Comp A. In the CT scan results, Comp B was the most effective surfactant as far as improvement in spontaneous imbibition is concerned. The use of Comp B also showed significant oil recovery from the core due to spontaneous imbibition as shown in Fig. 57.

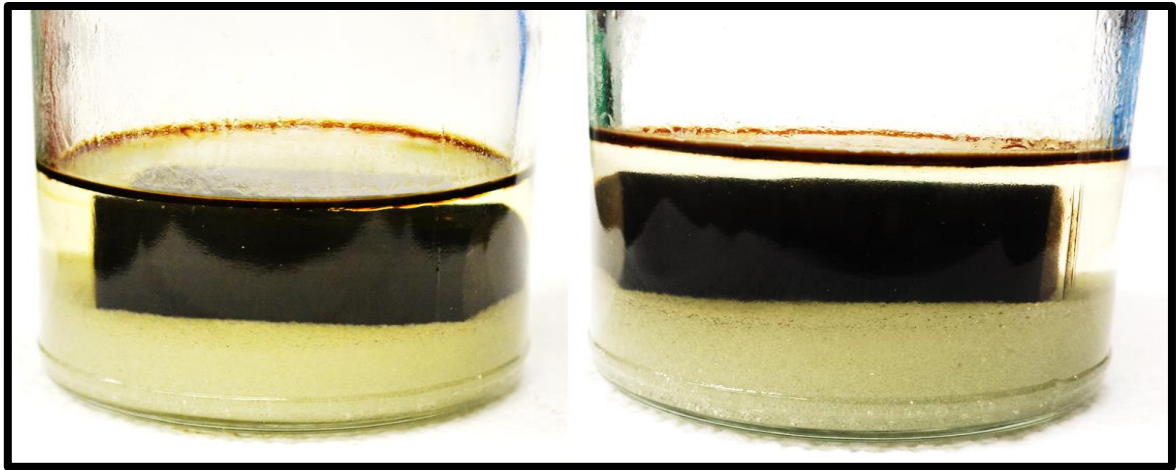


Fig. 57—Oil expelled from the shale core sample due to spontaneous imbibition of Comp B

6.2.3.5 Comp C

Fig. 58 shows the expulsion of oil from sample 6 due to spontaneous imbibition of brine enhanced with Comp C.

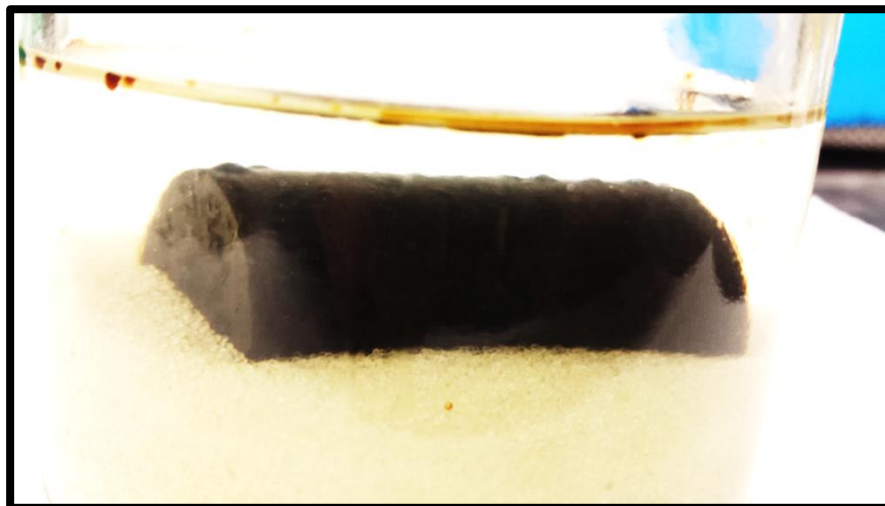


Fig. 58—Oil expelled from the shale core sample due to spontaneous imbibition of Comp C

6.2.3.6 Measured Oil Recovery

At the end of the experiment, oil expelled out of the sample was carefully transferred into graduated cylinders and measured. **Table 17** summarizes the oil recovery results. Although Surf B recovers the highest amount of oil, Comp B is more effective in improving the process of spontaneous imbibition since it is responsible for a higher change in oil saturation in sample 5. Surf A recovered the least amount of oil. Although, frac water did expel some oil droplets from sample 1, it was immeasurable. **Fig. 59** compares these oil recoveries for each surfactant side-by-side.

It is important to observe that the increase in water saturation in the core is higher than the change in oil saturation whereas theoretically, reduction in oil saturation should be equal to the increase in water saturation of the core. One plausible explanation for this discrepancy could be error in handling the recovered oil and measuring it accurately. However, the most likely reason for this difference is the fact that during the aging process, there is a possibility that not every pore space was saturated with oil. This might result in air remaining trapped inside the core sample which gets replaced by brine during the imbibition process. This pore volume is the difference between water imbibed and oil recovered.

The weights of the core samples were also measure for each experiment and although there is not enough data to conduct a material balance analysis, it can be observed that the weights after the experiments were higher as compared to before the experiments, regardless of the surfactant type. This indicates that brine, which has a

higher density than oil, has replaced the oil trapped in the pore spaces by the process of spontaneous imbibition.

Table 17—Summary of oil recoveries during spontaneous imbibition experiments

Sample #	Brine Content	Oil Recovery	Pore Volume	ΔS_o	ΔS_w from CT results	Weight (Before)	Weight (After)
		(cc)	(cc)	(%)	(%)	(g)	(g)
1	Frac Water	0.00	2.126	0.00%	3.28%	67.74	67.78
2	Surf A	0.07	1.299	5.39%	6.50%	33.30	33.43
3	Surf B	0.32	3.052	10.48 %	12.45%	68.91	69.21
4	Comp A	0.18	2.306	7.81%	10.62%	59.61	59.85
5	Comp B	0.24	2.127	11.3%	13.01%	53.21	53.48
6	Comp C	0.15	2.046	7.33%	9.99%	47.66	47.79

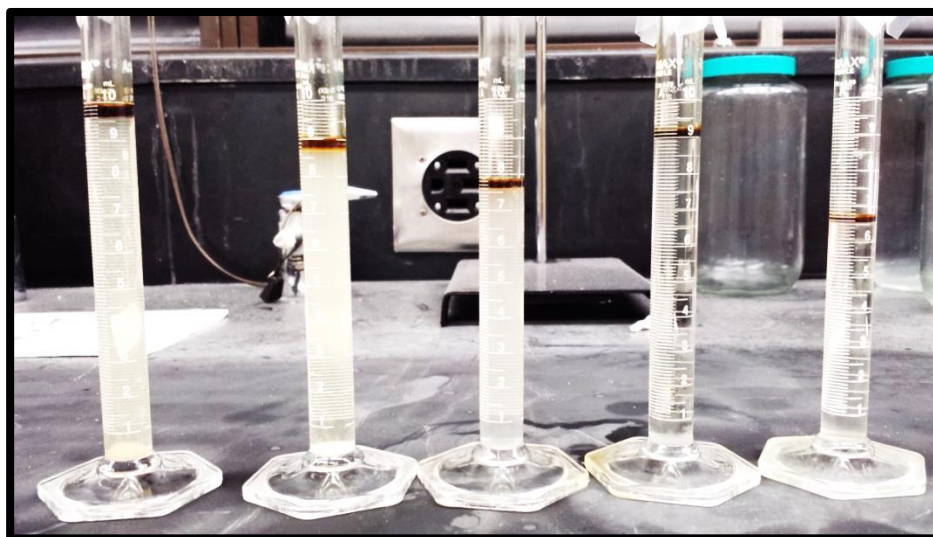


Fig. 59—Comparison of oil recoveries from different core samples due to spontaneous imbibition (L-R: Surf B, Comp B, Comp A, Comp C, and Surf A)

6.2.4 Summary of Results

Fig. 60 compares the change in CT response for each surfactant in the spontaneous imbibition experiments. It is very apparent that the addition of surfactant to the frac water results in bigger change in CT response due to improved imbibition.

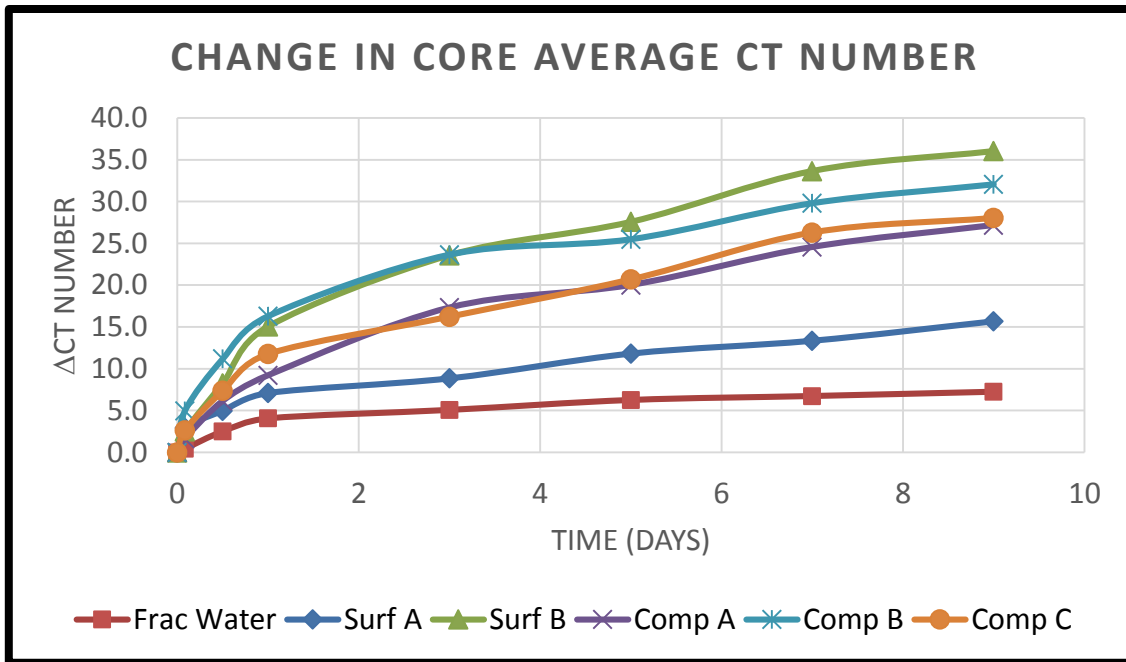


Fig. 60—Change in CT response due to addition of surfactants in brine

The CT scan and oil recovery results showed the importance of considering the effect of both wettability alteration and IFT reduction while investigating the potential of surfactants in improving spontaneous imbibition. Table 18 demonstrates the impact of wettability alteration and IFT reduction on capillary pressure for each surfactant. The table summarizes results from all the laboratory experiments. Eq. 3 was applied to calculate the capillary pressure for each surfactant due to a state of altered wettability

and reduced IFT at a sample shale pore throat. It is very interesting to see that the imbibition performance represented by the change in water saturation directly correlates to the capillary pressure of the system. Although these capillary pressure numbers are for static systems and are only representative, it provides an indication to the trend. Comp A was the most effective surfactant in altering wettability but the significant IFT reduction associated with it resulted in Comp A performing worse than Surf B and Com A in the spontaneous imbibition experiments. Surf B on the other hand, lowered the contact angle significantly but did not reduce the IFT of the system as much as the complex nano-surfactants. The capillary pressure of the system as a result, did not get drastically lowered and caused significant improvement in the imbibition process.

Table 18—Summary of results from all experiments

Sample #	Brine Content	Contact Angle	IFT	Pore Radius	Capillary Pressure	ΔS_w
		(°)	(mN/m)	(microns)	(psi)	(%)
1	Frac Water	110.1	21.78	0.13	-16.6971	3.28%
2	Surf A	72.20	9.82	0.13	6.696608	6.50%
3	Surf B	48.3	8.69	0.13	12.89575	12.45%
4	Comp A	35.3	3.86	0.13	7.027572	10.62%
5	Comp B	38	6.97	0.13	12.25235	13.01%
6	Comp C	46.6	4.79	0.13	7.341794	9.99%

In conclusion, it can be said that wettability alteration is not the only factor that impacts the potential of a surfactant in improving the performance of spontaneous imbibition. It is important to consider the effect of IFT reduction as well while choosing

a surfactant for oil recovery enhancement by the process of spontaneous imbibition. Among the five surfactants tested, CT scan and oil recovery results suggest that Surf B and Comp B are the best surfactants among nonionic and complex nano-surfactants respectively for use in stimulation fluids to improve oil recovery by better spontaneous imbibition.

7. NUMERICAL MODELING OF EXPERIMENTAL RESULTS

The main objective of this research work was to understand the impact of surfactants in shale reservoirs experimentally. However, in order to relate the impact of the results seen in the lab to wellhead performance, it is essential to resort to reservoir simulation to be able to numerically model the experimental results and use these models to predict the well head response. This section describes the methodology and results of the core scale reservoir simulation performed to model the surfactant imbibition mechanism.

7.1 Model Description

7.1.1 Introduction

A core scale model was built in the commercial ECLIPSE E100 simulator using the surfactant model. The use of the surfactant model was necessary in order to replicate the wettability alteration observed in the experiments. A radial grid was used to build the model. The porosity values of the cores ranged from 8.2% to 10.8% depending on the core in the experiment being modeled. The core permeability varied from 26 nD to 48 nD based on the special core analysis report. **Fig. 61** shows the model used in this simulation work. The outer grid cells shown in blue represent the cell in which the experiment was performed and the inner grid cells in green represent the core itself to its exact dimensions.

A pore volume multiplier was used for the outer grid cells to represent the volume of the container used in the experiment. The brine with or without surfactant is modeled to be initially present only in the outer grid cells and allowed to imbibe into the

core with time. End-point scaling was used for relative permeability tables in the simulation in order to scale relative permeability values based on specific end-points. The application of end-point scaling was essential since the initial water saturation in the experiments is close to zero while in the actual field, this fact might not hold true. Therefore, the use of end-point scaling allowed for the change in initial water saturation depending on the scenario.

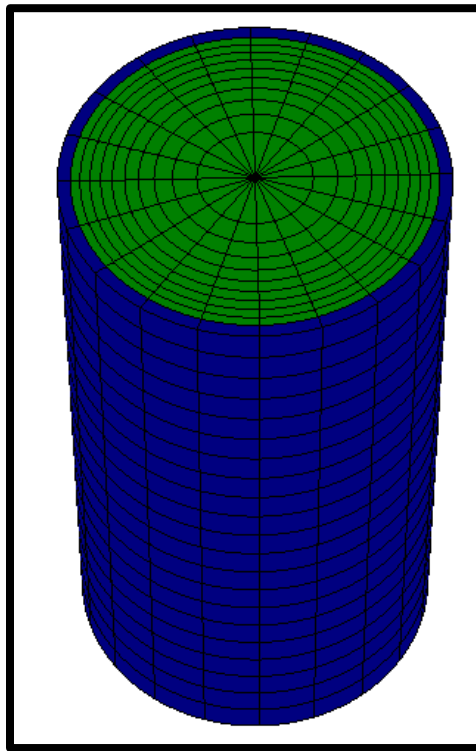


Fig. 61—Core scale simulation model used to model imbibition experiments

7.1.2 Modeling Wettability Alteration

This sub-section describes the specific parameters that were used in order to model the process of wettability alteration in the simulation model. The simulation

model depicting the spontaneous imbibition experiment with Surf B is used as a representation for all models. It is important to understand that these parameters were changed for each different surfactant experiment studied. *Section 2.5* provides the theoretical discussion of how a simulator models wettability alteration.

ECLIPSE E100 simulator was used in this study as previously mentioned. In order to model wettability alteration, the simulator requires two different sets of relative permeability and capillary pressure tables, one indicating the state of native wettability while the other indicating a state of altered wettability. Based on the adsorption of surfactant in a grid block which in turn is dependent on the concentration in a particular grid block, the simulator interpolates between these two sets of saturation functions in order to model the change in wettability. Since actual experiments to measure the adsorption were not conducted, the Langmuir isotherm approach was implemented to model the adsorption of surfactant on rock.

7.1.3 Model Calibration

The objective of this study was to obtain a calibration between the lab results and a numerical model. Typically, while modeling spontaneous imbibition experiments in conventional systems, oil recovery during the experiment acts as the main history matching parameter. Unfortunately, oil recoveries could not be measured during these experiments due to the added complexity of shales. However, CT analysis of these experiments provided information about the change in water saturation during the experiments. Therefore, core water saturation was used as the primary history matching parameter to calibrate the numerical model. History matching was performed solely by

altering the capillary pressure tables since capillary pressure is the best indicator of wettability in a numerical model.

The first step was to calibrate the numerical model to the CT response of the experiment performed with brine or frac water without any surfactant. The saturation functions which provide a history match in this scenario would indicate the native wettability of the rock and hence becomes the first set of relative permeability and capillary pressure curves for all the other experiments involving surfactants. The second set of saturation functions which indicate a state of altered wettability was obtained for each specific surfactant through rigorous history matching altering the capillary pressure curves.

7.2 Results and Discussion

This sub-section presents and discusses the results for each spontaneous imbibition experiment performed in the laboratory in the previous section.

7.2.1 Frac Water

The simulation model describing the spontaneous imbibition response of frac water without any surfactant was unique due to the fact that it did not require any wettability alteration modeling. However, it was important to get a good history match in this model since it formed the baseline for spontaneous imbibition in shales without any surfactant. **Fig. 62** shows the history match obtained for water saturation between the actual CT results and the simulation model by altering the capillary pressure curve in the model.

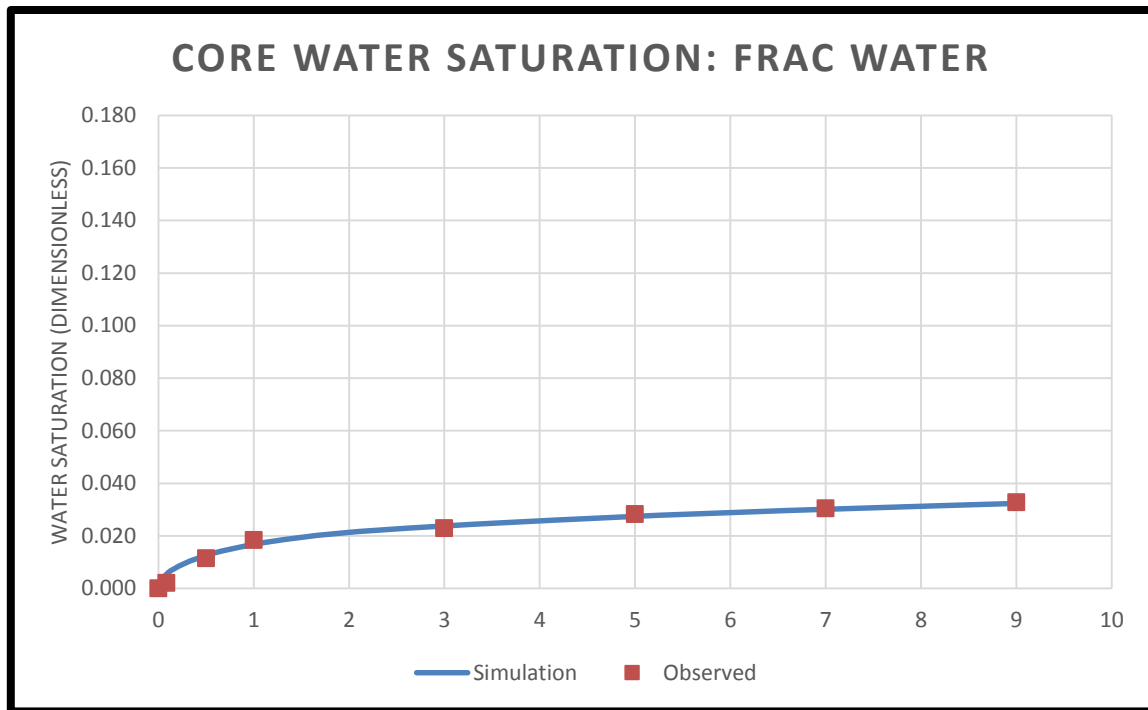


Fig. 62—Water saturation history match for frac water

7.2.2 Surf A

Fig. 63 shows the history match obtained for Surf A. In this case, wettability alteration was modeled and two sets of capillary pressure curves were provided. The first set of capillary pressures was obtained from the history match of the frac water case while the second set of capillary pressures was obtained from history matching in this model.

Surf A performed the worst among all the surfactants in terms of the extent of wettability alteration. This behavior was successfully modeled in the simulation and matched with the CT response.

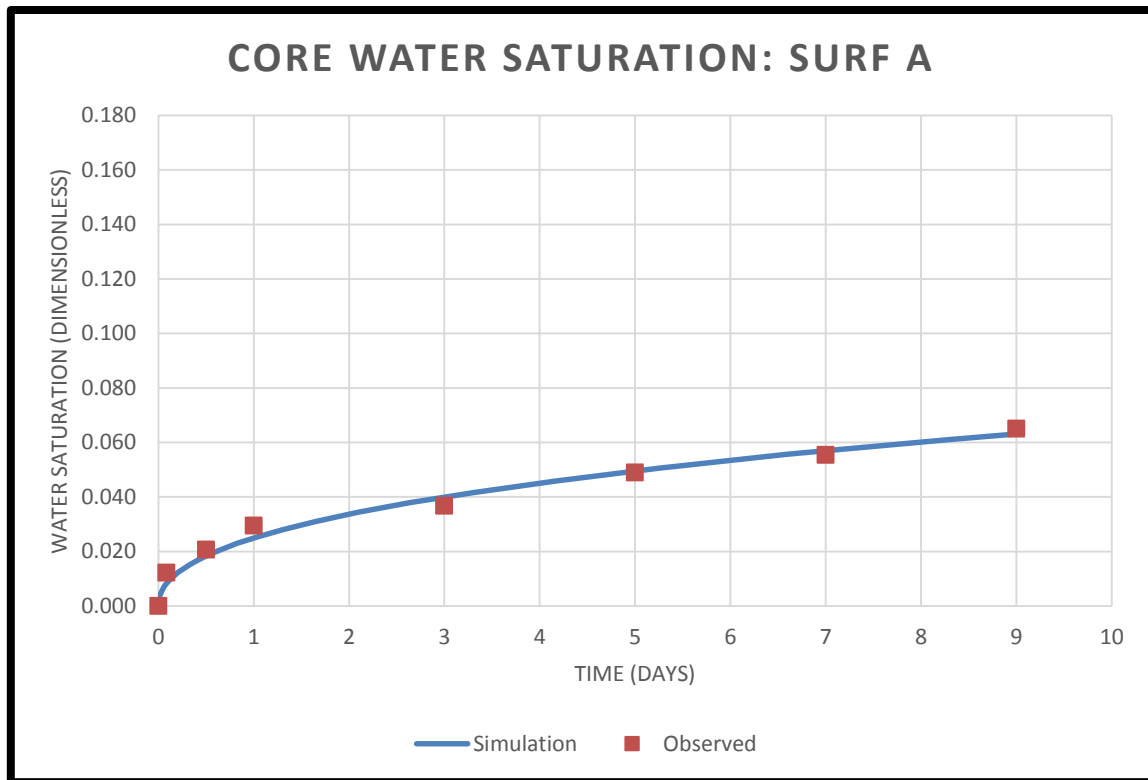


Fig. 63—Water saturation history match for Surf A

7.2.3 Surf B

CT analysis showed much higher water saturation change in Surf B as compared to Surf A. Wettability alteration combined with a modest reduction in IFT resulted in higher capillary pressures which favored spontaneous imbibition of water into the matrix. **Fig. 64** shows the water saturation history match obtained for Surf B.

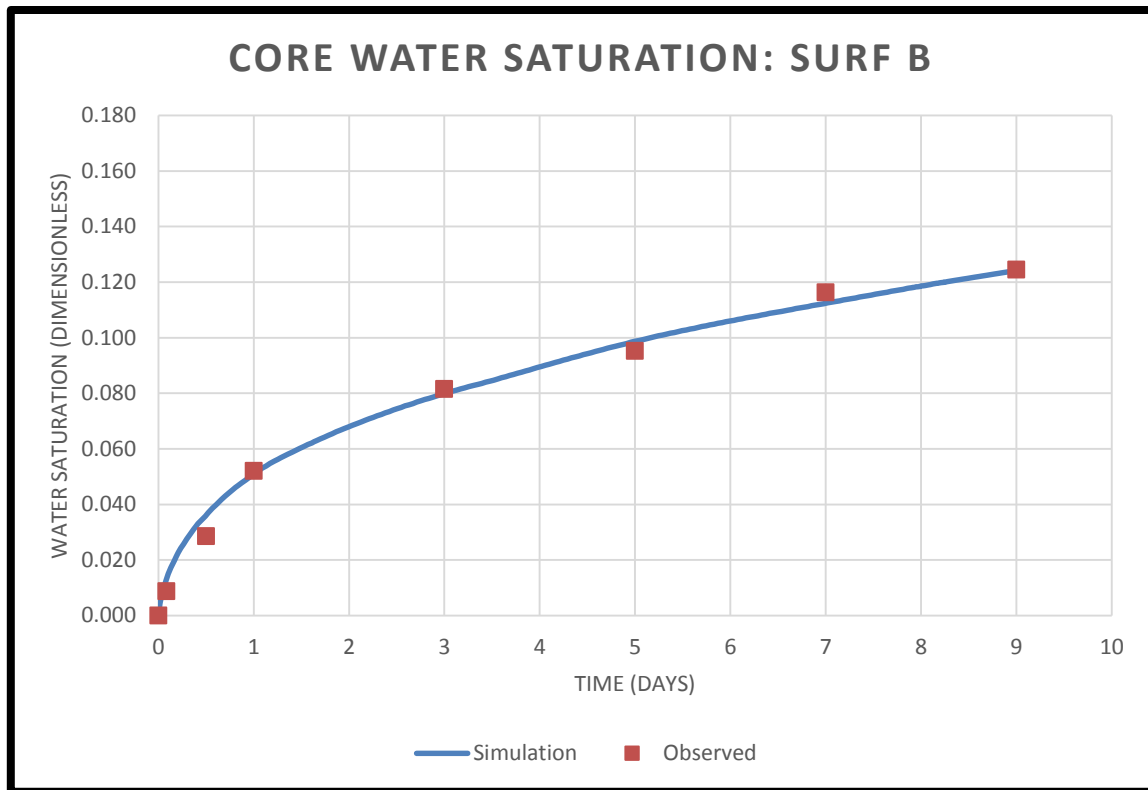


Fig. 64—Water saturation history match for Surf B

7.2.4 Comp A

In general, the complex nano-surfactants altered wettability of shale more effectively than the nonionic surfactants. However, CT analysis showed mixed results of spontaneous imbibition performance. **Fig. 65** shows the water saturation history match for Comp A. The imbibition performance of Comp A was worse than that of Surf B and the final water saturation chance after 9 days was 10.6% as compared to 12.45% in the Surf B case.

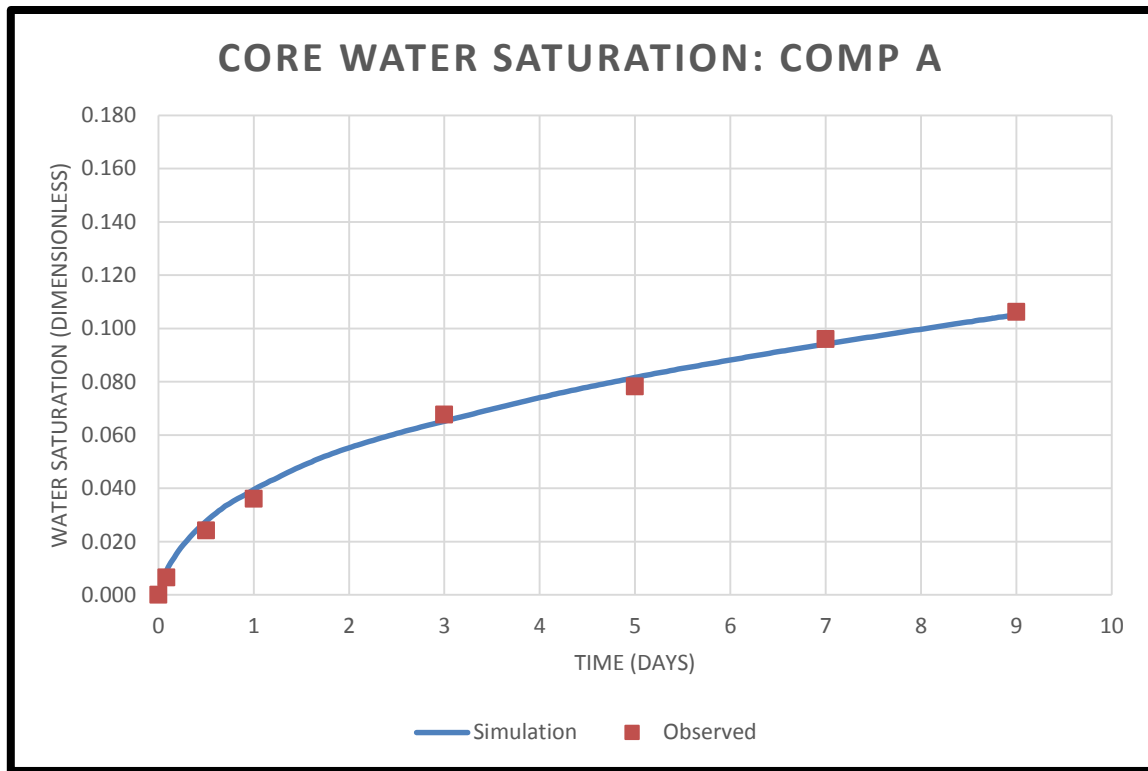


Fig. 65—Water saturation history match for Comp A

7.2.5 Comp B

Comp B was the best performing surfactant among all the tested surfactants which showed the maximum increase in water saturation at the end of the spontaneous imbibition experiment. **Fig. 66** shows the water saturation history match for Comp B. The final change in water saturation was calculated as 13.01%. Significant alteration in wettability combined with only a modest reduction in IFT as compared to Comp A and Comp B as summarized in Table 18 resulted in high capillary forces which favored efficient imbibition of water into the matrix.

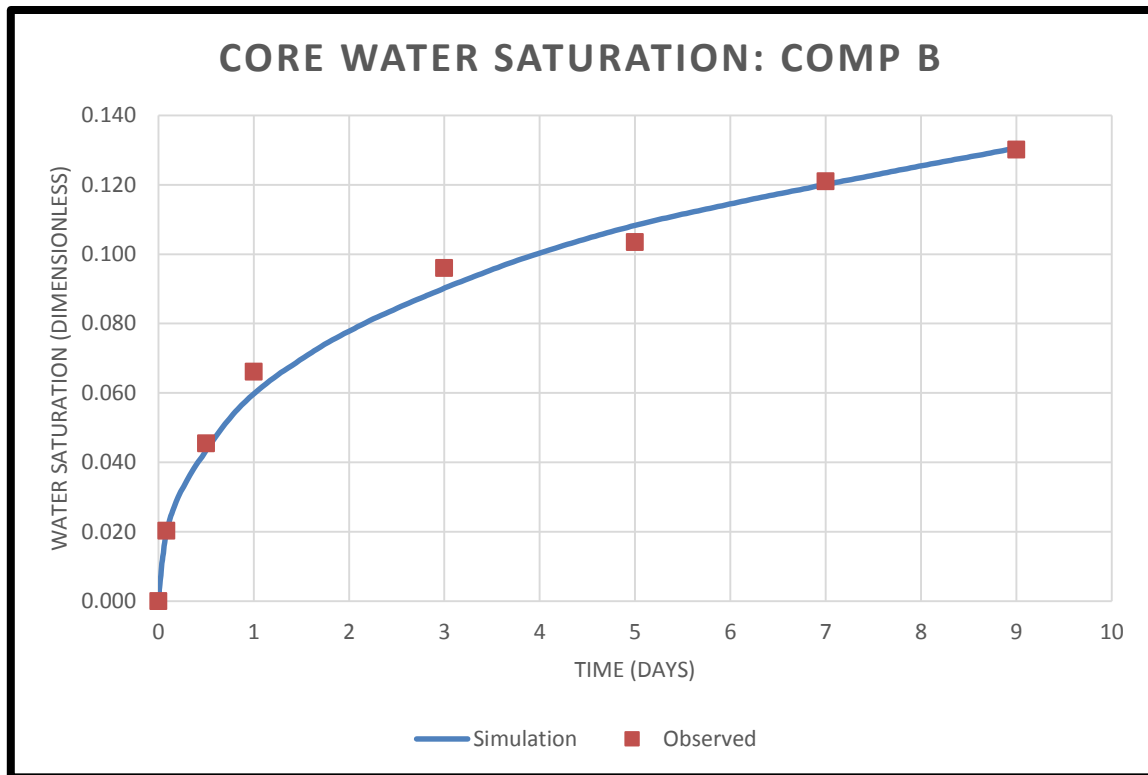


Fig. 66—Water saturation history match for Comp B

7.2.6 Comp C

Comp C was slightly less performing than Comp A in the spontaneous imbibition experiments achieving a final change in water saturation of around 9.99%. **Fig.67** shows the water saturation history match for Comp C. Comparing all the surfactants, only Surf A performed poorer than Comp C in the spontaneous imbibition experiments.

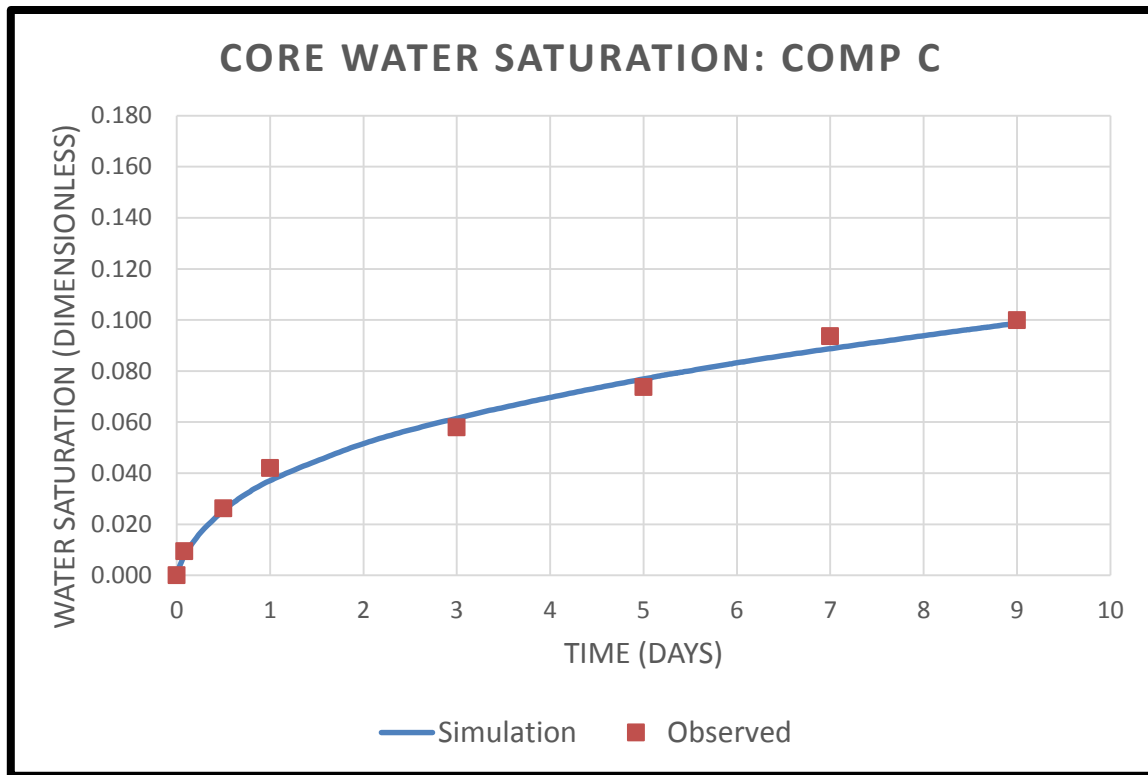


Fig. 67—Water saturation history match for Comp C

7.2.7 Capillary Pressure Curves Modeling Altered Wettability

As mentioned previously, the history matching was performed by supplying a capillary pressure function to the simulator which modeled the state of altered wettability due to the presence of surfactant. **Fig. 68** shows the history matched capillary pressure curves used to match water saturation in the experiments for all cases. **Table 19** presents the same information in a tabular form. In the model involving only frac water without any surfactant, the capillary pressure obtained after calibration reiterated the intermediate state of wettability of the shale rock with capillary pressure values ranging

from slightly positive to largely negative values in the water saturation domain. This capillary pressure curve acted as the baseline for all the other simulation runs.

For the simulation models involving surfactants, the mechanism of wettability alteration was captured by interpolating the capillary pressures between the native wettability capillary pressures obtained from the frac water case and a set of altered wettability capillary pressures. This set of capillary pressures representing altered wettability was different for each surfactant as shown in Table 19. The history matches shown in Figs. 63-67 were obtained using the capillary pressure curves shown in Fig. 68 respectively.

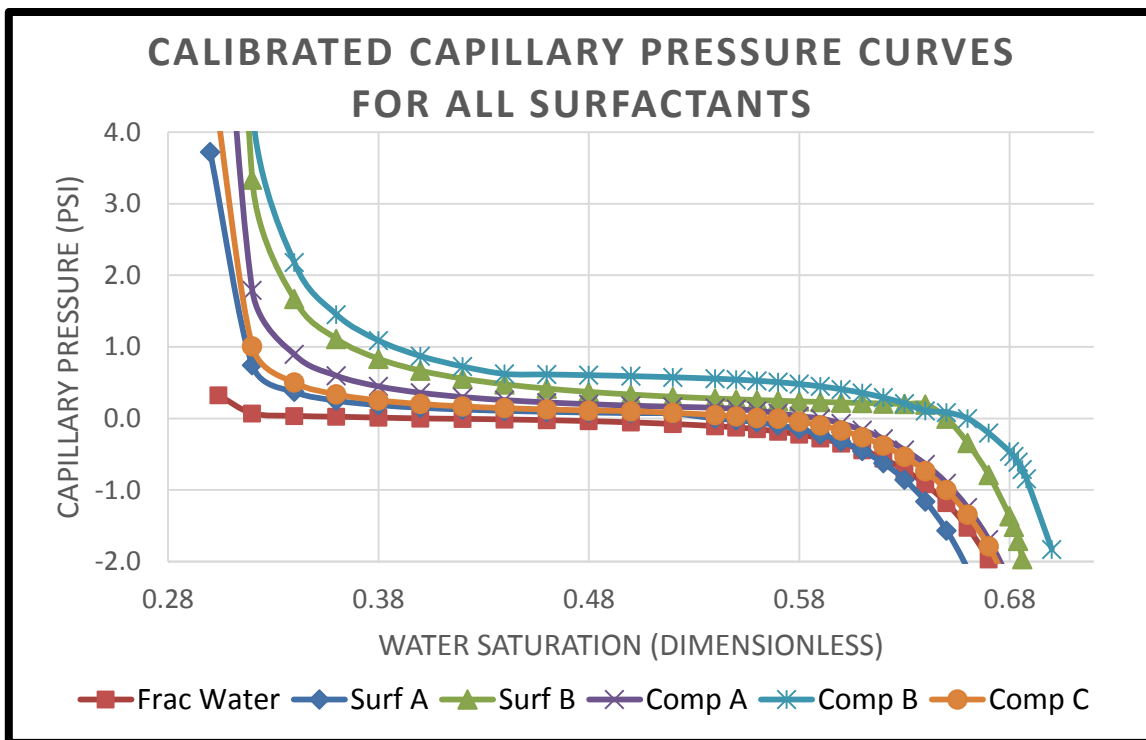


Fig. 68—History matched capillary pressure curves for all surfactants

Table 19—Calibrated capillary pressure values for all surfactants

Sw	Capillary Pressure (psi)					
	Frac Water	Surf A	Surf B	Comp A	Comp B	Comp C
0.30	0.323	3.723	16.684	8.954	21.788	5.040
0.32	0.072	0.745	3.337	1.791	4.358	1.008
0.34	0.036	0.372	1.668	0.895	2.179	0.504
0.36	0.024	0.248	1.112	0.597	1.453	0.336
0.38	0.012	0.186	0.834	0.448	1.089	0.252
0.40	0.SPE-	0.149	0.667	0.358	0.872	0.202
0.42	-0.006	0.124	0.556	0.298	0.726	0.168
0.44	-0.014	0.106	0.477	0.256	0.623	0.144
0.46	-0.024	0.093	0.417	0.224	0.614	0.126
0.48	-0.038	0.083	0.371	0.199	0.604	0.112
0.50	-0.055	0.074	0.334	0.179	0.591	0.101
0.52	-0.078	0.068	0.303	0.163	0.575	0.078
0.54	-0.107	0.SPE-	0.278	0.149	0.555	0.049
0.55	-0.126	-0.023	0.267	0.130	0.542	0.030
0.56	-0.151	-0.055	0.257	0.105	0.526	0.005
0.57	-0.183	-0.096	0.247	0.073	0.506	0.SPE-
0.58	-0.225	-0.151	0.238	0.031	0.480	-0.042
0.59	-0.280	-0.225	0.230	0.SPE-	0.448	-0.096
0.60	-0.350	-0.322	0.222	-0.071	0.407	-0.167
0.61	-0.443	-0.452	0.215	-0.163	0.356	-0.259
0.62	-0.562	-0.624	0.209	-0.283	0.291	-0.379
0.63	-0.718	-0.854	0.202	-0.438	0.210	-0.535
0.64	-0.920	-1.159	0.196	-0.641	0.107	-0.737
0.65	-1.184	-1.565	0.SPE-	-0.904	0.085	-1.001
0.66	-1.526	-2.105	-0.342	-1.246	0.SPE-	-1.343
0.67	-1.970	-2.823	-0.787	-1.691	-0.205	-1.787
0.68	-2.549	-3.778	-1.365	-2.269	-0.463	-2.365
0.68	-2.699	-4.032	-1.515	-2.419	-0.529	-2.516
0.68	-2.894	-4.370	-1.711	-2.615	-0.611	-2.711
0.69	-3.148	-4.819	-1.965	-2.869	-0.714	-2.965
0.69	-3.479	-5.417	-2.295	-3.199	-0.844	-3.295
0.70	-6.054	-10.186	-4.871	-5.775	-1.829	-5.871

7.2.8 Summary of Results

In summary, the core scale surfactant simulation model was able to replicate the spontaneous imbibition experiments fairly well. The models were calibrated with the experimental results using capillary pressure tables signifying native and altered states of wettability. Although conventional measurements such as oil recovery during the spontaneous imbibition experiment were not available, proper CT analysis allowed for the calculation of change in water saturation which was used as the primary history matching parameter.

Overall, this section highlighted the effort in representing the experimental findings of this study using a numerical approach. The ultimate step in this study is to use these core scale numerical results in a larger well scale model in an attempt to estimate the improvement in performance at the wellhead due to wettability alteration by surfactants in shales which is described in the next section.

8. NUMERICAL INVESTIGATION OF THE EFFECT OF SURFACTANT ON WELL PERFORMANCE USING A SINGLE WELL FRAC MODEL

The primary objective of this entire study was to investigate the potential of surfactants added to frac fluid in improving oil recovery in ultra-tight shales by the process of spontaneous imbibition. The experimental results and the core scale modeling results are of very little use unless they are incorporated in a model which replicates an actual hydraulic fracturing job performed on a well. This section highlights the work performed to build a single well hydraulic fracturing model calibrated to actual field data and describes the use of this calibrated model to understand the impact of surfactant on well performance after the hydraulic fracturing operation.

8.1 Model Description

Accurate modeling of hydraulic fracturing in shales is challenging since the aspects of geomechanical changes during frac operations need to be incorporated in these models. Such a model is complicated and requires significant computing resources. Since the primary objective of this study was not to really investigate the performance of a hydraulic fracturing operation but to compare frac fluids with and without surfactants, a geomechanical model was considered superfluous. A calibrated single well model which models the load injection and recovery and a stimulated rock volume region (SRV) due to the frac job was used along with a surfactant model to estimate the impact of surfactant added to the frac fluid on the well performance. This sub-section briefly describes the single well frac model.

8.1.1 Single Well Frac Model

The hyper threaded simulator, tNavigator, developed by Rock Flow Dynamics (RFD) was used to build and run this model. The model built for this study incorporates two clusters of fractures on one size of a horizontal well. Instead of modeling all the clusters of each fracture stage, only two clusters were modeled to save on computational time. In order to estimate the total productivity of the well, the production of the two clusters in the model was multiplied accordingly accounting for identical production from the remaining clusters. **Fig. 69** shows water saturation in the model at the end of frac load injection. The model designates a particular region close to the wellbore as the SRV in which proppant gets placed during the frac operation. The permeability of this region is higher than that of the rest of the formation. The fracture half-length (x_f) was determined as 165 ft from fracture maps. The permeability, height and width of the SRV region were determined from history matching.

The porosity and permeability of the shale formation in the simulation were 9.65% and 20 nD respectively. These values of porosity and permeability were largely representative of the range of values reported in the special core reports and indicate an ultra-tight shale matrix system as discussed throughout this entire study.

A small porosity of 1% was used for the SRV in the model since it is packed with proppant subjected to massive rock stresses. A rock compaction model was also used in the simulation which allowed for the change in the pore volume and transmissibility of a grid block as a function of changing pressure.

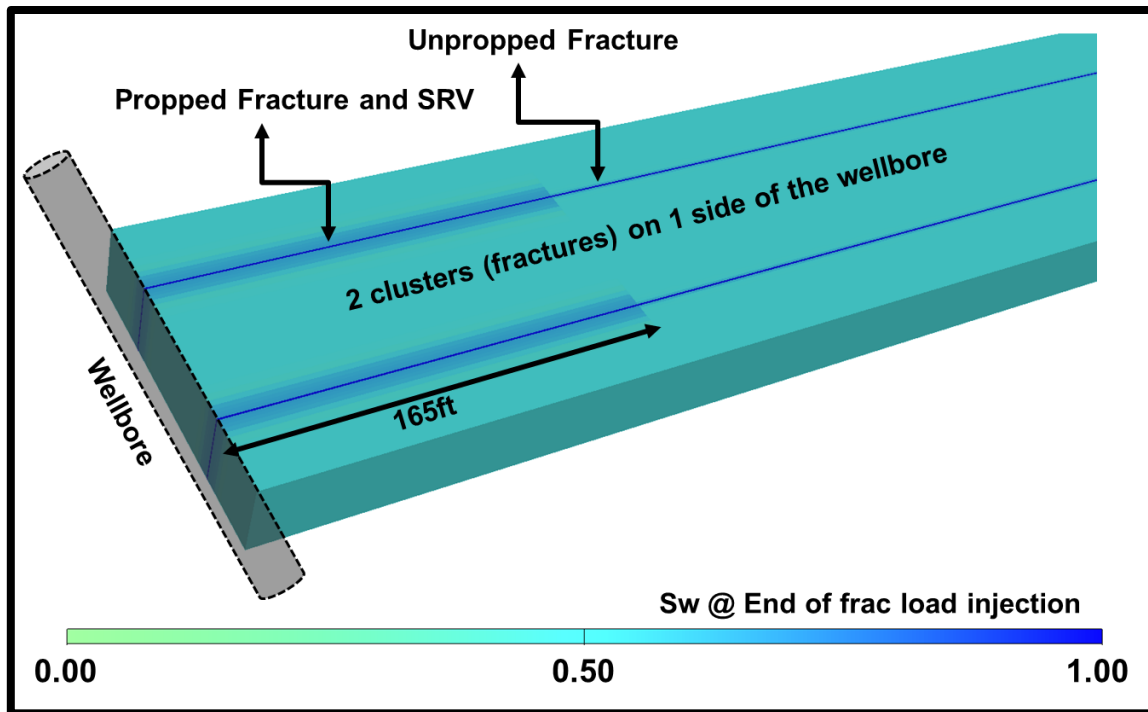


Fig. 69—Description of the single well frac model

8.1.2 PVT and Rock Properties

PVT analysis was performed on crude samples collected from this particular well in the laboratory. The results from the PVT report were incorporated in the simulation model. The model in total had four components — oil, water, gas, and dissolved gas. The relative permeability tables for the matrix and SRV region in the model were derived from the core scale model. Stick relative permeability curves indicating flow in fracture were used for the cells representing the fractures. End-point scaling was implemented in this model and the connate water saturation of the matrix was set at 50%. The surfactant parameters used in this model are identical to those used in the core scale model. Surfactant adsorption was modeled using a Langmuir isotherm.

8.1.3 Model Calibration

Actual production data for two years was available for this well. The single well frac model was calibrated with this observed data before implementing the surfactant model. The primary parameters that were altered to obtain a history match were height, width, and permeability of the SRV. A total fluid rate constraint was enforced in the simulation and the primary history matching objectives were to match the oil rate, pressure, water cut, and GOR.

Fig. 70 shows the final history match obtained for the model. The height and width of the SRV region in the calibrated model was 150 ft. and 21 ft. respectively. The permeability of this region was enhanced as compared to the matrix and the history match was obtained with a permeability of 500 nanodarcies. The early time pressure response was not fully calibrated as three neighboring vertical wells communicated with this well during that time. A similar event was recorded near the end of history where the water cut could not be matched as interference of two vertical well ‘fracs’ resulted in higher than expected water production in this well.

Overall, the simulation model was fairly well calibrated to actual data allowing further implementation of the surfactant model to estimate the change in wellhead performance due to wettability alteration in the rock matrix.

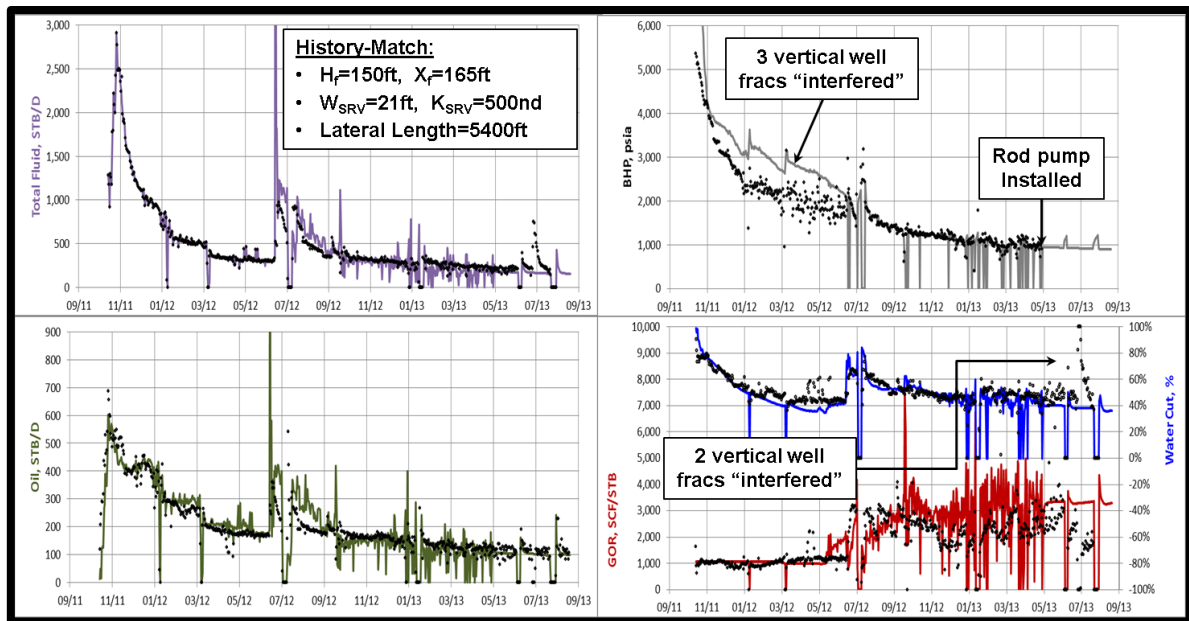


Fig. 70—Final history match plots

8.2 Results and Discussion

8.2.1 Surfactant Model Implementation

After successfully calibrating the single well frac model, the surfactant model was added to the frac model to allow for wettability alteration due to the addition of surfactant to the frac fluid. The surfactant was introduced to the rock system as a part of the frac fluid during the load injection process. Fig. 71 shows the successful placement of surfactant in the SRV after the end of load injection. This shows that the surfactant model was functioning correctly allowing for wettability alteration in the rock matrix based on the surfactant concentration. The concentration of surfactant in the frac fluid was kept constant at 2.0 gpt.

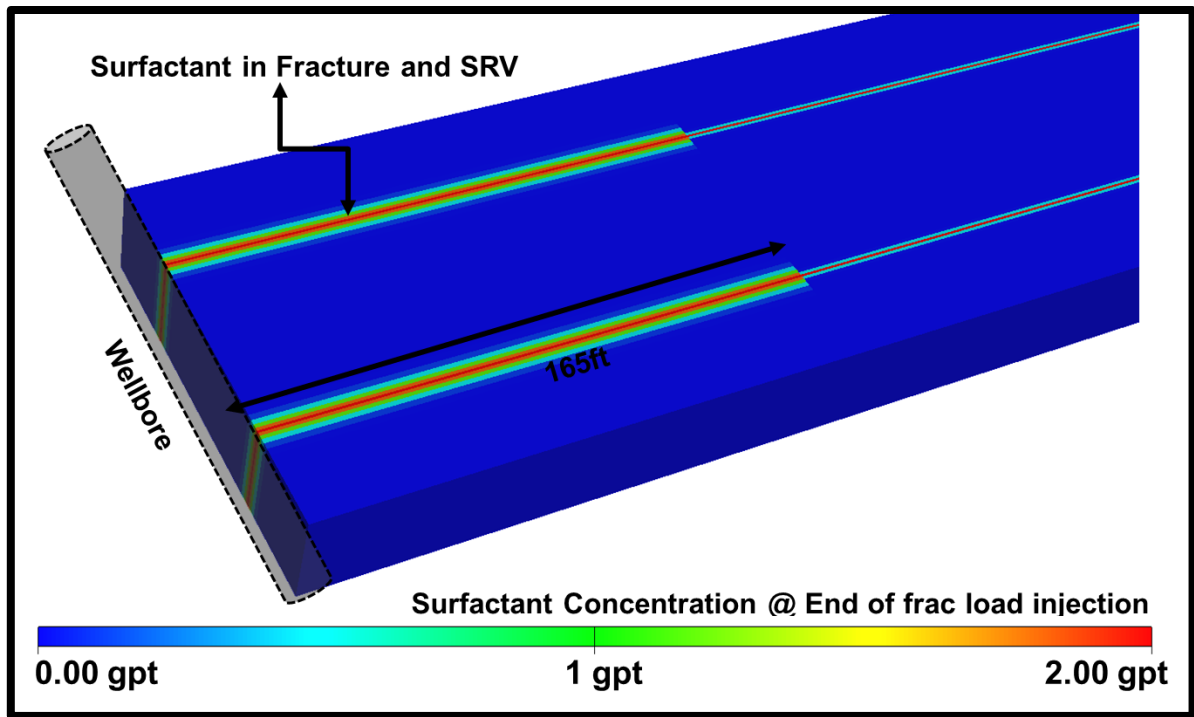


Fig. 71—Surfactant placement at the end of the frac load injection

8.2.2 Role of Surfactant in Changing Wellhead Performance

Once it was ascertained that the surfactant model is working correctly and the surfactant is being placed in the SRV during the frac load injection, it was interesting to investigate the role of this surfactant in altering wettability and its impact on wellhead performance.

Fig. 72 compares the cumulative oil production of the base case (frac water only) and all the different surfactant cases. It was extremely surprising to observe that a state of altered wettability due to surfactant addition to the frac fluid actually hurt the wellhead performance and decreased the cumulative oil production. The dashed line represents the actual production data while the red curve indicates the well calibrated base case. The cumulative oil production curve for every surfactant superimposes one another

indicating that the extent of wettability alteration is not very sensitive to wellhead performance during primary production post hydraulic fracturing. In any case, it is clear that the use of any surfactant in frac fluid which altered the state of wettability to strongly water-wet conditions resulted in poorer performance and lower cumulative oil production. This result was surprising and counterintuitive especially considering the impressive results seen with surfactants in the laboratory experiments. Hence, further analysis was required to ensure the validity of this observation.

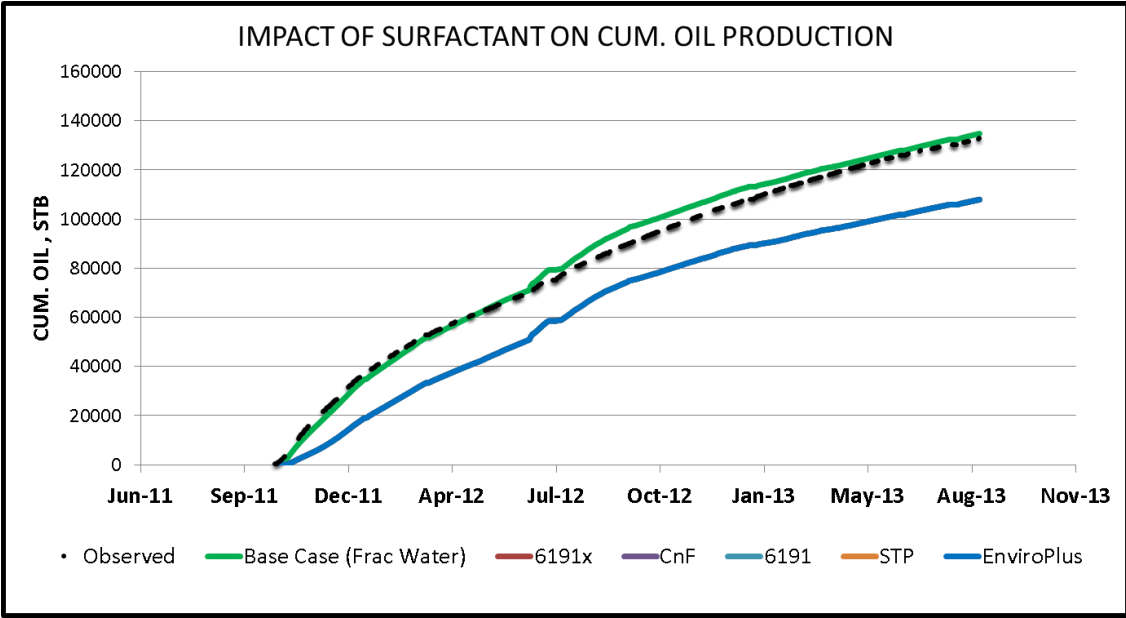


Fig. 72—Comparison of cumulative oil recoveries of all simulation cases

8.2.3 Additional Investigation to Understand Impact of Wettability Alteration on Wellhead Performance Post Hydraulic Fracturing

It was observed that wettability alteration resulted in poor primary production post hydraulic fracturing. On the other hand, addition of surfactant to frac water resulting in wettability alteration in the rock improved oil production due to enhanced spontaneous imbibition performance in the lab. In order to explain this difference in performance, it is important to understand the oil recovery mechanisms involved in the lab experiments and in the field.

The lab experiment involved placing an aged shale core in a cell containing frac water with or without surfactant. The sole oil recovery mechanism in this experiment is spontaneous imbibition as there is no pressure drawdown applied to the core sample. The addition of surfactant resulted in alteration of wettability in the shale sample enhancing the mechanism of spontaneous imbibition and hence, improving the oil recovery. A plausible explanation to why a similar improvement in oil recovery is not seen in the single well frac model could be the fact that the oil recovery mechanism in this case is different.

Wettability alteration only helps improve performance when imbibition activity occurs. For imbibition to occur, the wetting phase has to be available in abundance in the system like in a waterflooding scenario. In a typical hydraulic fracturing operation, water amounting to only a very small percentage of the pore volume, is pumped during load injection. The surfactant was added to this frac water during load injection which altered the wettability of the rock surface that it came in contact with. However, after recovery

the load and popping the well open, no additional water was available in the SRV to promote any further imbibition due to the altered state of wettability. The dominant oil recovery mechanism in the fractured well is the fluid expansion due to the applied pressure drawdown. A state of strongly water-wet wettability results in water spreading on the inner surface of the pore trapping the oil molecules in the center of the pore space. In such a scenario, the pressure drawdown finds it difficult to overcome this additional capillary force exerted due to a state of preferential wettability and get the fluids out of the pore space. Hence, the addition of surfactant to frac water results in lower cumulative oil production.

It is important to understand the difference in the oil recovery mechanisms exhibited in the lab experiments and in the field. **Fig. 73** shows the loss in cumulative oil production due to wettability alteration by calculating the difference in cumulative oil production between the surfactant and the frac water case at each time step. The addition of surfactant to frac water lowers the oil production starting day 1 and the trend continues during the entire simulation with a higher decline at early time.

In order to verify the explanation provided above, a simple modification was made to the simulation model. An additional injector was placed in the model close to the SRV region. After the completion of load recovery, water injection for two additional months was performed before the well was popped. **Fig. 74** shows the location of this new well in the model. Simulation runs were performed with this added feature for both the frac water and surfactant cases.

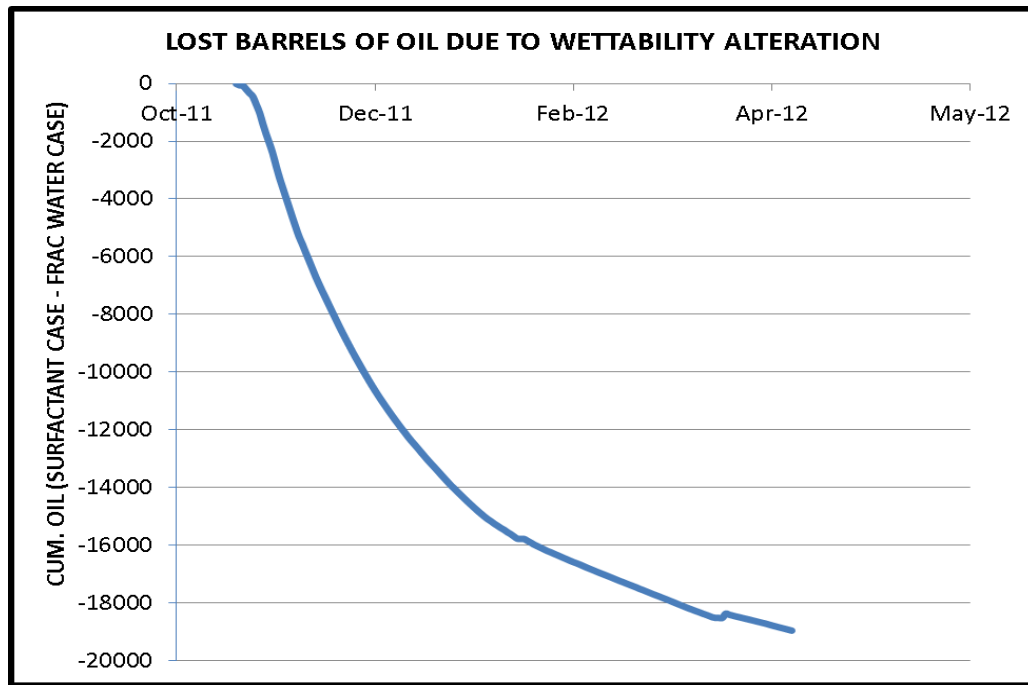


Fig. 73—Loss of production due to addition of surfactant to frac water

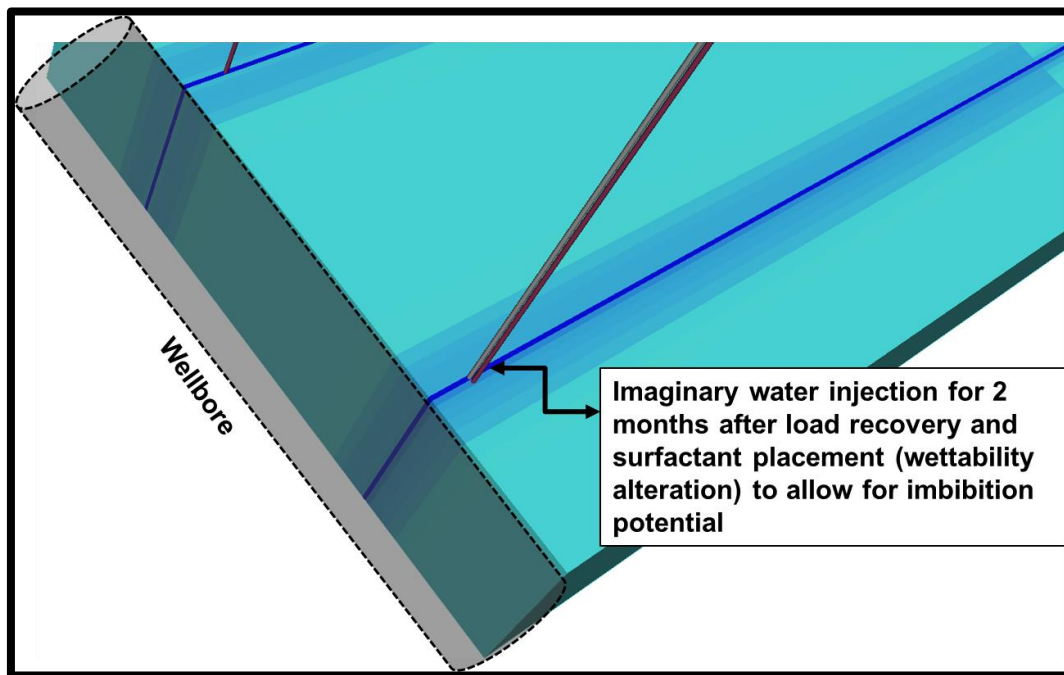


Fig. 74—Additional injector close to the SRV region

The results from the new simulation runs with additional water injection were compared. **Fig. 75** shows the same comparison for the new simulation runs as that shown in Fig. 74. It was observed that the additional water injection after load recovery but prior to production resulted in better cumulative oil production in the surfactant case as compared to the frac water case. This observation verifies the explanation proposed above. Unlike in the previous comparison, the presence of additional water in the SRV after wettability alteration due to surfactant resulted in improved spontaneous imbibition leading to better initial oil recovery in the surfactant case as compared to frac water case.

The difference in cumulative oil recovery between the surfactant and frac water cases increases initially but soon starts to decrease as the rate of imbibition slows down after water injection ceases. At some point in time, oil recovery due to fluid expansion exceeds the oil recovery due to improved spontaneous imbibition and hence, the difference in cumulative oil between the surfactant and frac water cases becomes negative.

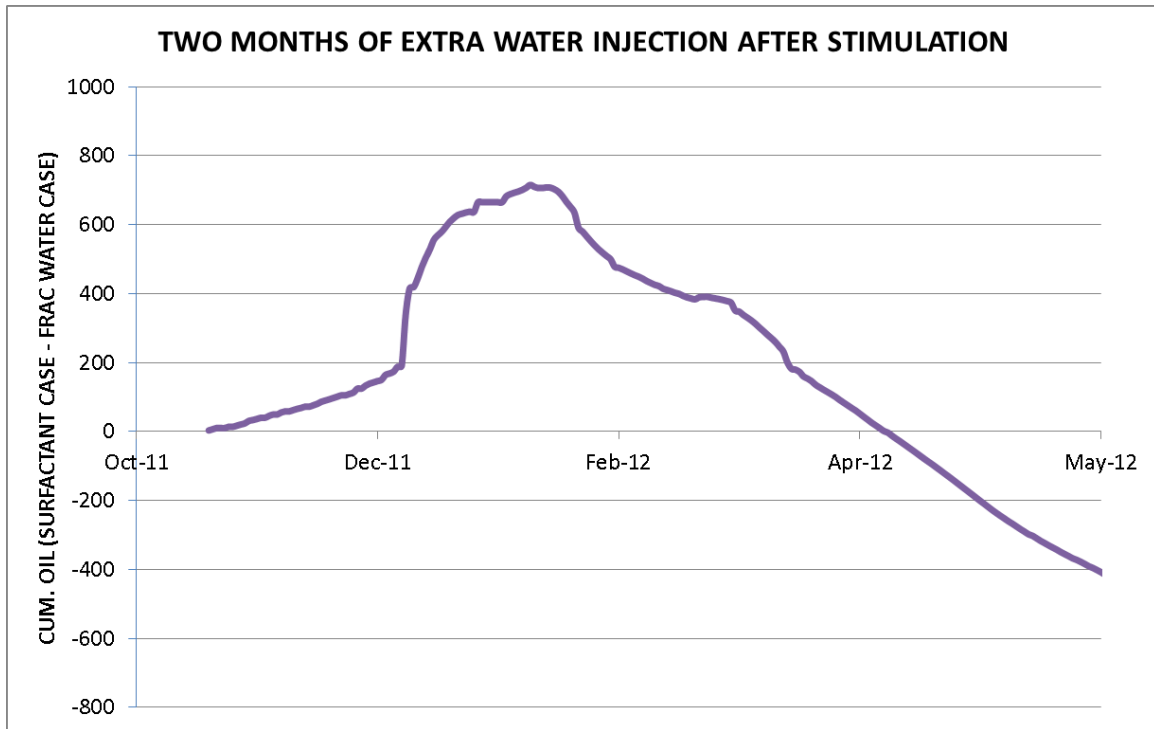


Fig. 75—Impact of additional water injection on cumulative oil production

In summary, additional water injection after wettability alteration allows oil recovery due to spontaneous imbibition. This effect results in increased oil production during the initial phase of production. However, in time, this effect fades away and hurts oil production at middle/late time due to oil being trapped in the pore space. Wettability alteration has shown to help improve oil production in the lab due to enhanced spontaneous imbibition but it does not improve the performance of a well after hydraulic fracturing unless additional injection is performed to supply water to allow for imbibition to occur and recover additional oil.

9. CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

This study was performed to investigate the potential of surfactants in stimulation fluids to alter wettability of ultra-tight oil-rich shale formations and improve oil recovery after well stimulation. The study began with lab experiments in which the potential of several different surfactants in altering wettability in these shale formations was studied. Thereafter, these experimental findings were modeled at a core scale to understand the process of capturing wettability alteration by surfactants in a numerical model. Lastly, the results from the core scale simulation model were used in a larger single well frac model to estimate the impact of surfactant and wettability alteration on wellhead performance post hydraulic fracturing. The following conclusions were reached after the completion of this study:

- a) Contact angle experiments demonstrated that the native state of wettability of this shale formation is intermediate-wet and surfactants have the potential to alter the wettability to preferentially water-wet conditions.
- b) Addition of surfactant to frac fluid also reduces the IFT of the system depending on the concentration and type of surfactant used. IFT reduction lowers the effectiveness of wettability alteration in improving oil recovery by spontaneous imbibition.
- c) Spontaneous imbibition experiments using CT methods showed that surfactant enhanced brines recovers significantly more oil than frac water alone due to improved spontaneous imbibition. Surf B and Comp B

performed the best out of all the surfactants due to significant wettability alteration but modest IFT reduction associated with these two surfactants resulting in the creation of strong capillary forces.

- d) The process of wettability alteration and associated improvement in oil recovery was successfully modeled numerically in the simulator with the help of a surfactant model using different sets of capillary pressure curves signifying states of native and altered wettability.
- e) The single well frac model was able to simulate the response of the reservoir after hydraulic fracturing accurately. However, the addition of surfactant to the frac fluid hurt the performance of the well and lowered cumulative oil recovery due to additional capillary force as a result of preferential wettability in the system.
- f) The discrepancy between the lab results and the results from the single well frac model stems in the fact that the primary oil recovery mechanisms in these two cases are not identical. Spontaneous imbibition is the only oil recovery mechanism responsible for oil recovery in the lab. On the other hand, most of the oil post hydraulic fracturing in the field is recovered due to fluid expansion resulting from an applied pressure drawdown. Additional capillary force due to a state of preferential wettability counteracts the viscous force resulting in lower recovery due to addition of surfactant.
- g) Surfactants have shown to have the potential of altering wettability in oil-rich shales and improving oil recovery by the process of spontaneous imbibition.

However, the unavailability of conditions in the reservoir required for spontaneous imbibition post well stimulation results in the failure of useful application of wettability alteration through stimulation fluids.

9.2 Recommendations

It is important to understand that any study involving ultra-tight shales is challenging and this type of research is work in progress. Conventional approaches to research typically fail while dealing with such tight rocks. Hence, it is essential that a novel approach is pursued instead of resorting to conventional ideas since conventional techniques usually do not apply to ‘unconventional’ reservoirs. Based on the experience gained in this study, following recommendations are proposed for future scope of work:

- a) Subjecting core samples to vacuum prior to aging is highly recommended as it would eliminate trapped air in the core sample and help perform accurate CT response analysis.
- b) Dean Stark method can also be applied to have a better idea of the contents of the core sample prior to the aging process.
- c) The spontaneous imbibition experiments should be run for longer durations under the CT scanner to identify the endpoint of spontaneous imbibition since the imbibition rate in these tight rocks is very slow.
- d) Surfactant adsorption can be measured in the lab in order to build a more robust simulation model.
- e) The single well frac model can be improved further by incorporating the geomechanical aspects of hydraulic fracturing.

- f) The impact of wettability alteration by surfactant on oil production should be studied in other scenarios such as surfactant EOR in shales.

NOMENCLATURE

bopd	Barrels of oil per day
cm	Centimeter
cp	Centipoise
CMC	Critical micelle concentration
COBR	Crude oil/brine/rock
CT	Computed tomography
° F	Degree Fahrenheit
EOR	Enhanced oil recovery
EUR	Estimated ultimate recovery
FOV	Field of view
GOR	Gas oil ratio
gpt	gallons per thousand gallons
IFT	Interfacial tension
md	Millidarcy
mg	Milligram
mN/m	Millinewton / meter
ppm	Parts per million
S_{wi}	Initial water saturation
SRV	Stimulated rock volume
USBM	United States Bureau of Mines

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